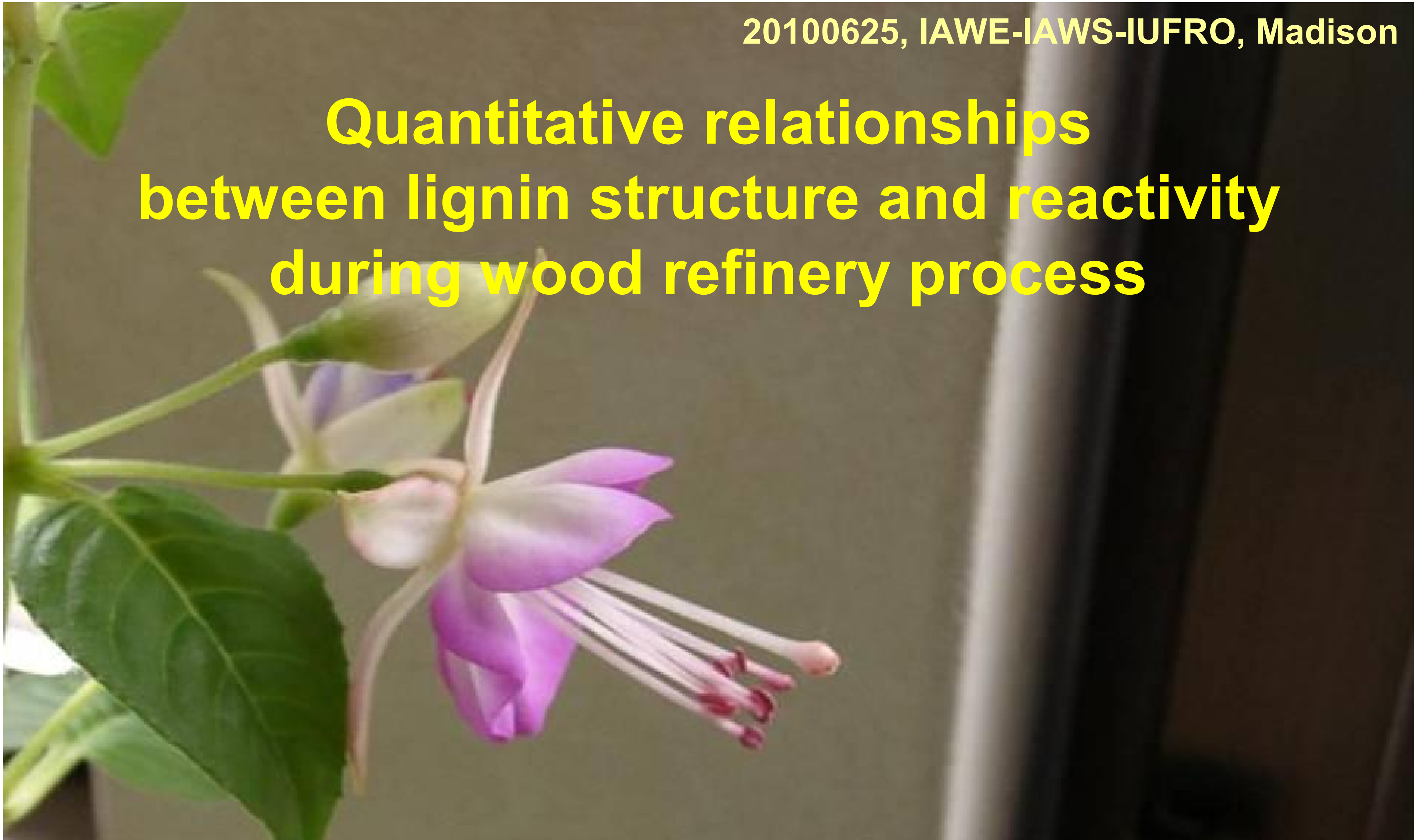
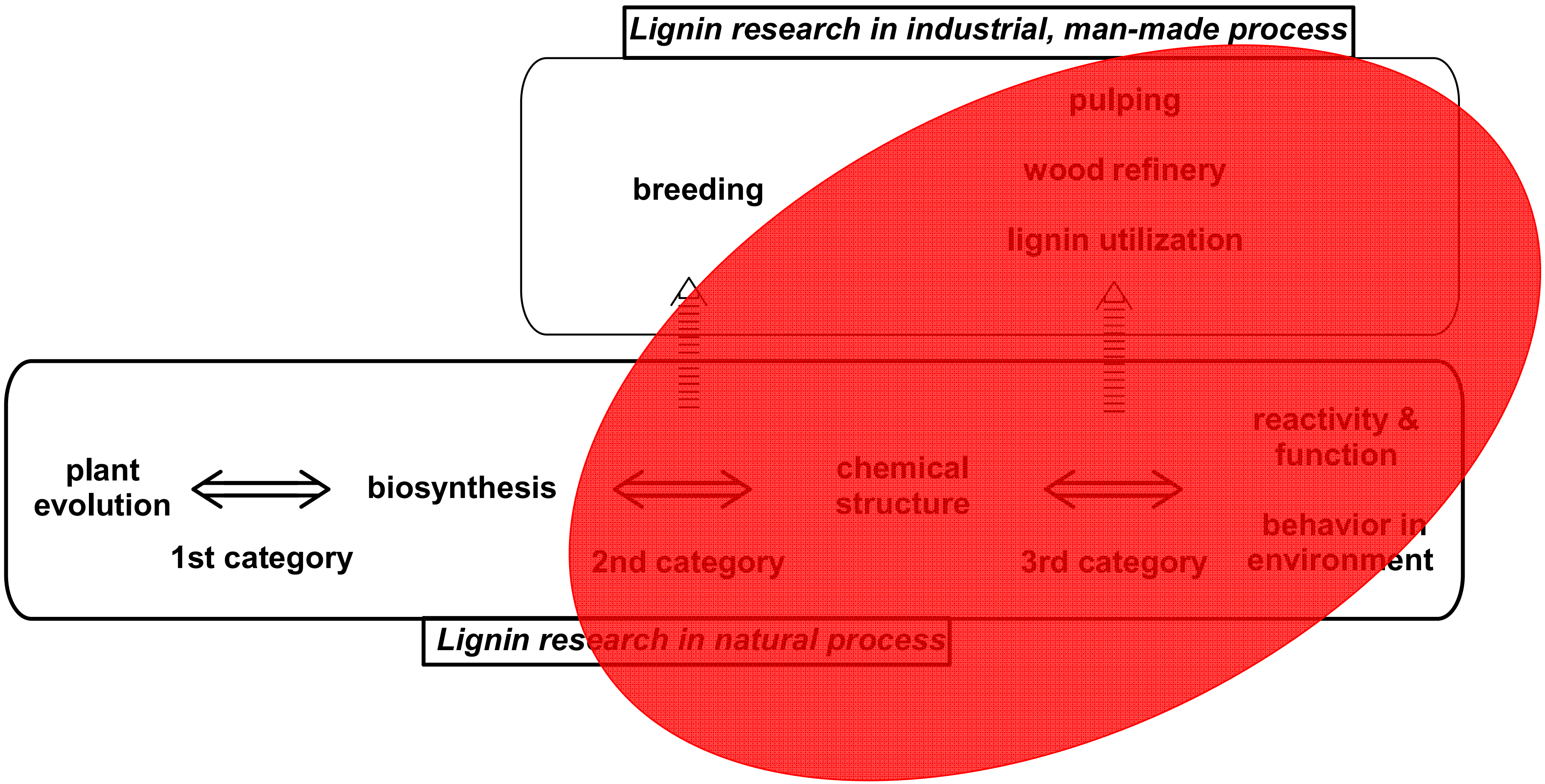
20100625, IAWE-IAWS-IUFRO, Madison

Quantitative relationships between lignin structure and reactivity during wood refinery process



Yuji Matsumoto
Wood Chemistry Laboratory, The University of Tokyo

What is the rule when the nature creates woody cell wall?



First, we have to see how the nature creates plant cell wall.

What is the rule when the nature designed cell wall?

Wide variety of lignin structure and amount

low or high lignin content?

aromatic ring type?

phenolic or non-phenolic?

interunit linkages?

amount of β-O-4 strucutre?

stereo structure of β-O-4?

etc

so many factors which could affect reactivity of lignin !

Wide variety of lignin structure and amount

low or high lignin content? **16 – 38%**

aromatic ring type?

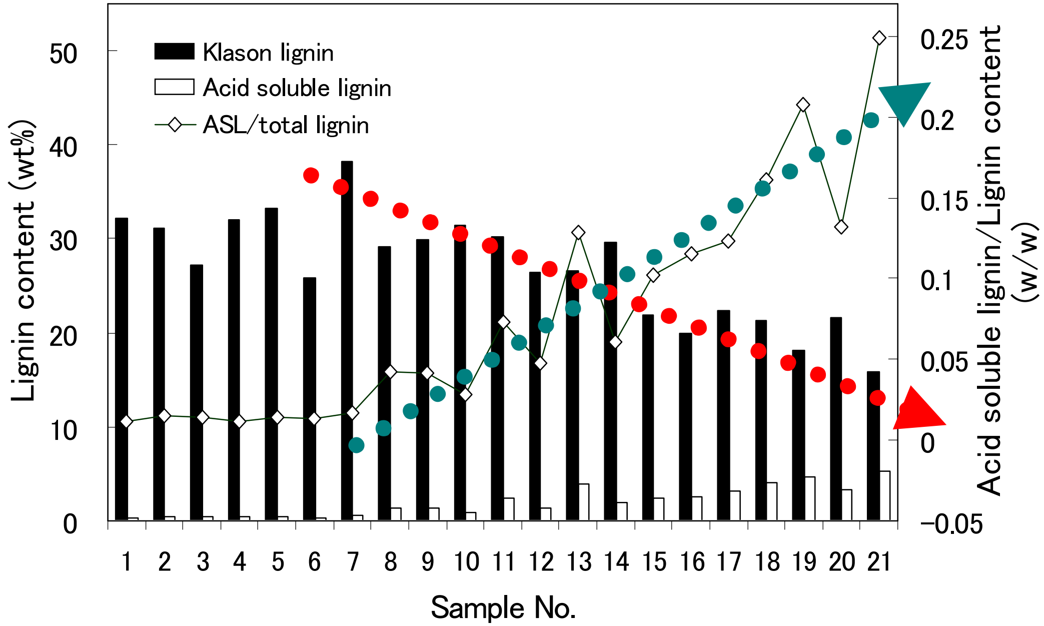
phenolic or non-phenol

interunit linkages?

amount of β-O-4 strucu

stereo structure of β-O-

etc



more methoxyl group in lignin

so many factors which could affect reactivity of lignin !

Wide variety of lignin structure and amount

low or high lignin content?

aromatic ring type?

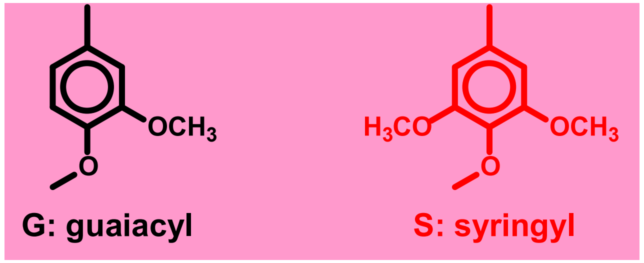
phenolic or non-phenolic?

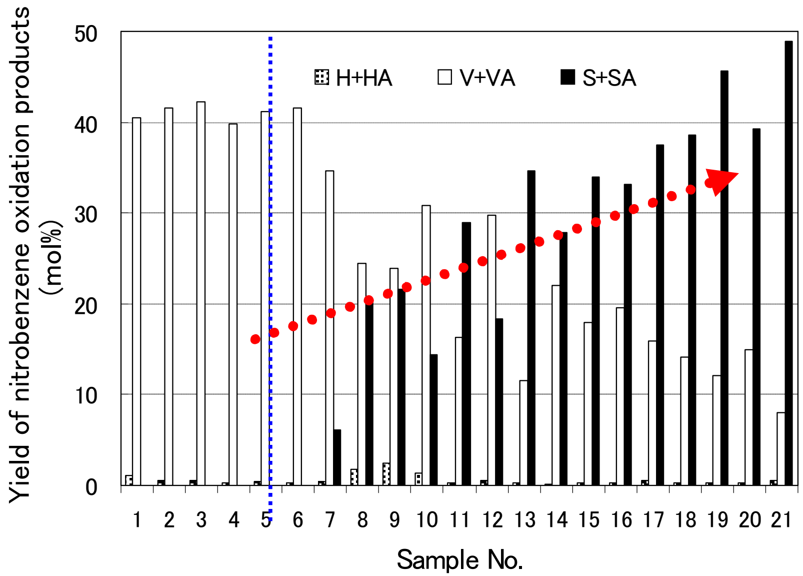
interunit linkages?

amount of β-O-4 strucutre?

stereo structure of β-O-4?

etc



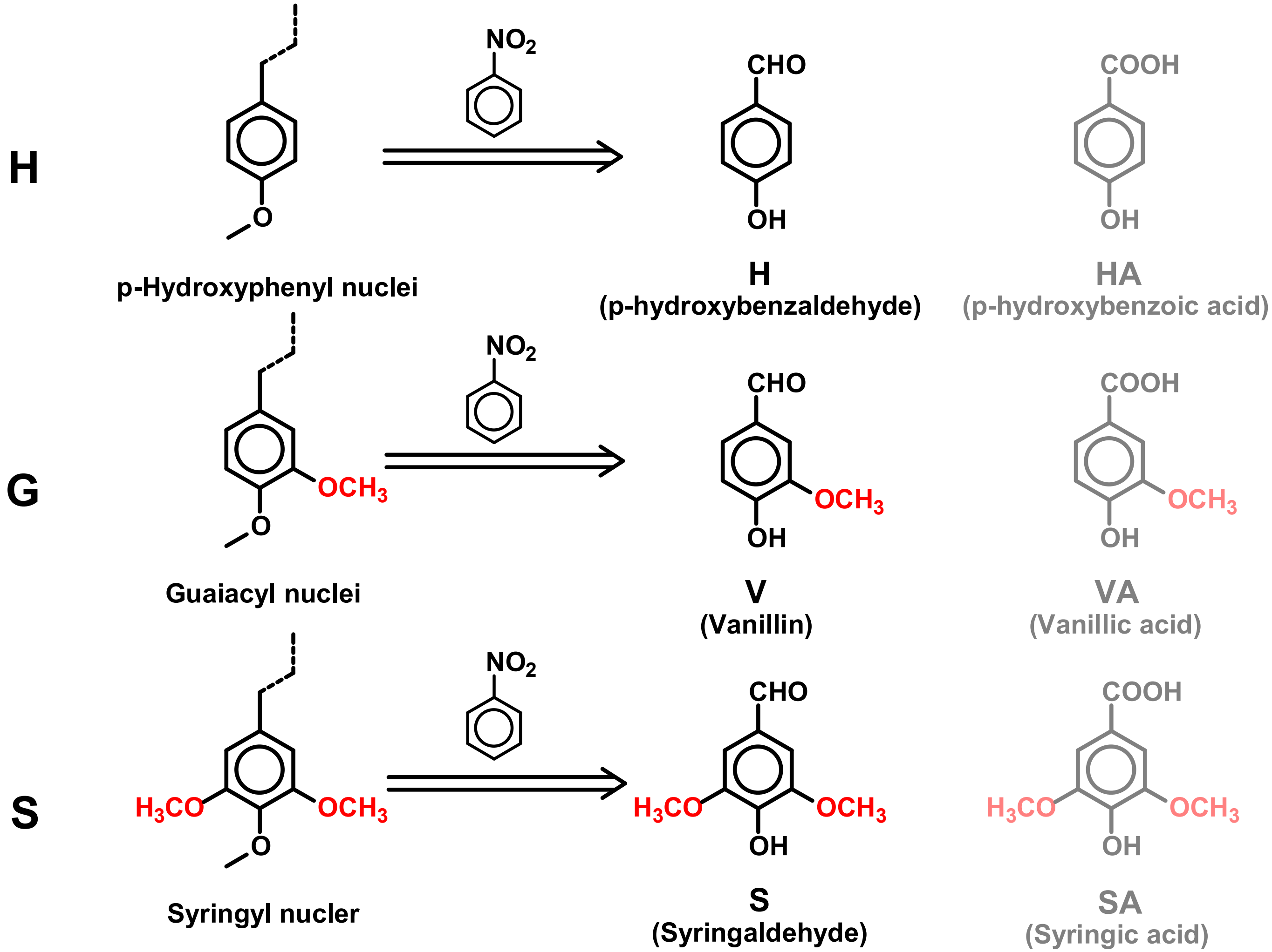


more methoxyl group in lignin

S/G: 0 – 5

so many factors which could affect reactivity of lignin !

method to analyze aromatic ring type

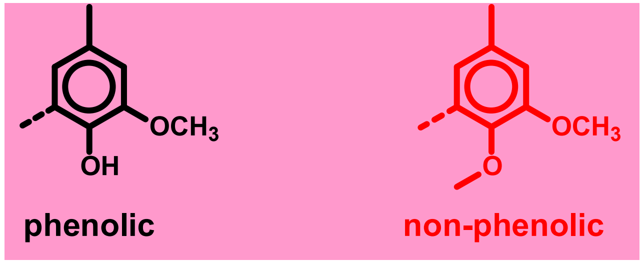


syringyl ratio: S / (S+G)

Nitrobenzene oxidation

S/G ratio: S / G

Wide variety of lignin structure and amount



low or high lignin content?

aromatic ring type?

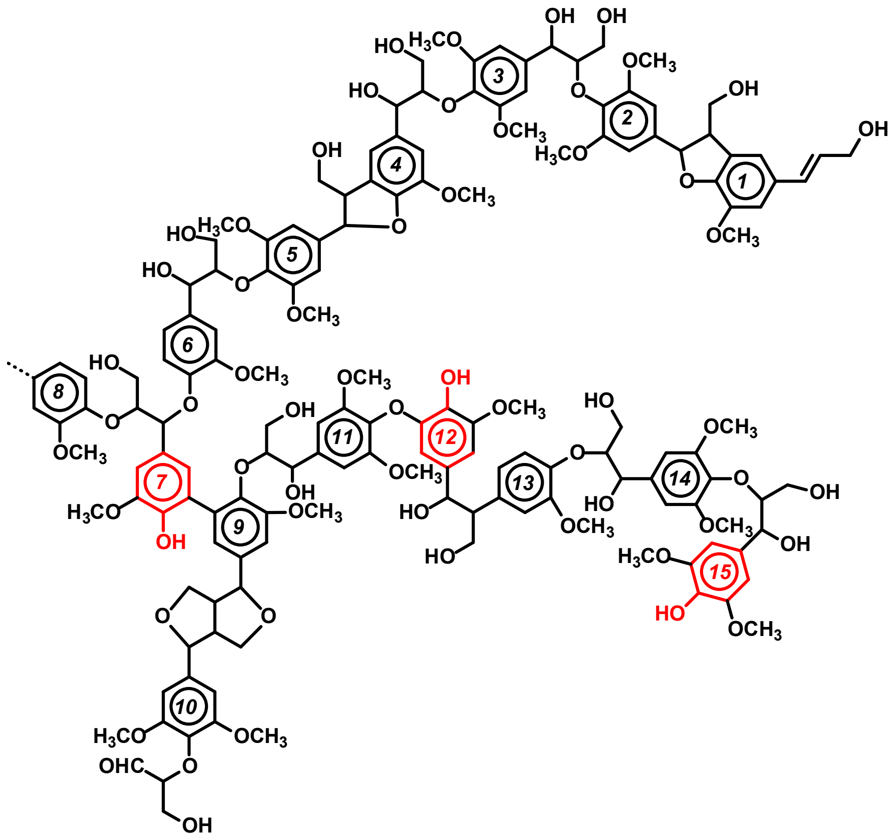
phenolic or non-phenolic?

interunit linkages?

amount of β-O-4 strucutre?

stereo structure of β-O-4?

etc



so many factors which could affect reactivity of lignin !

Wide variety of lignin structure and amount

low or high lignin content?

aromatic ring type?

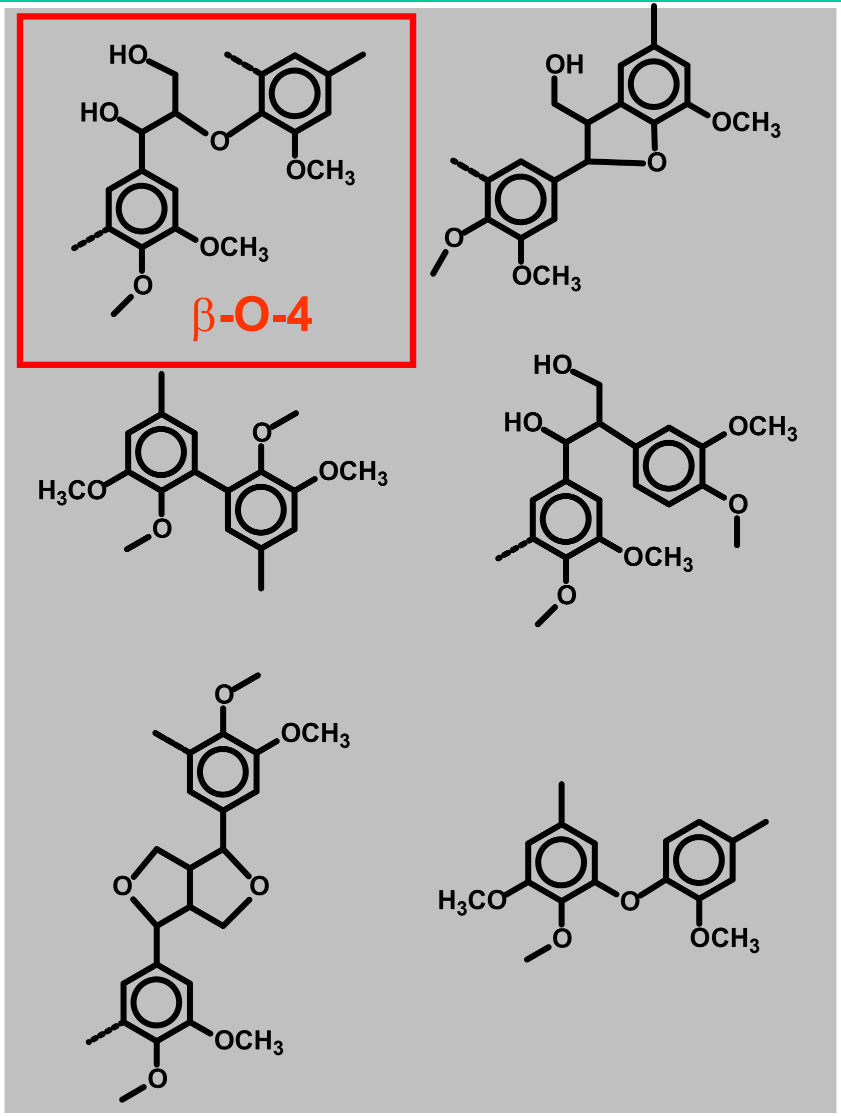
phenolic or non-phenolic?

interunit linkages?

amount of β-O-4 strucutre?

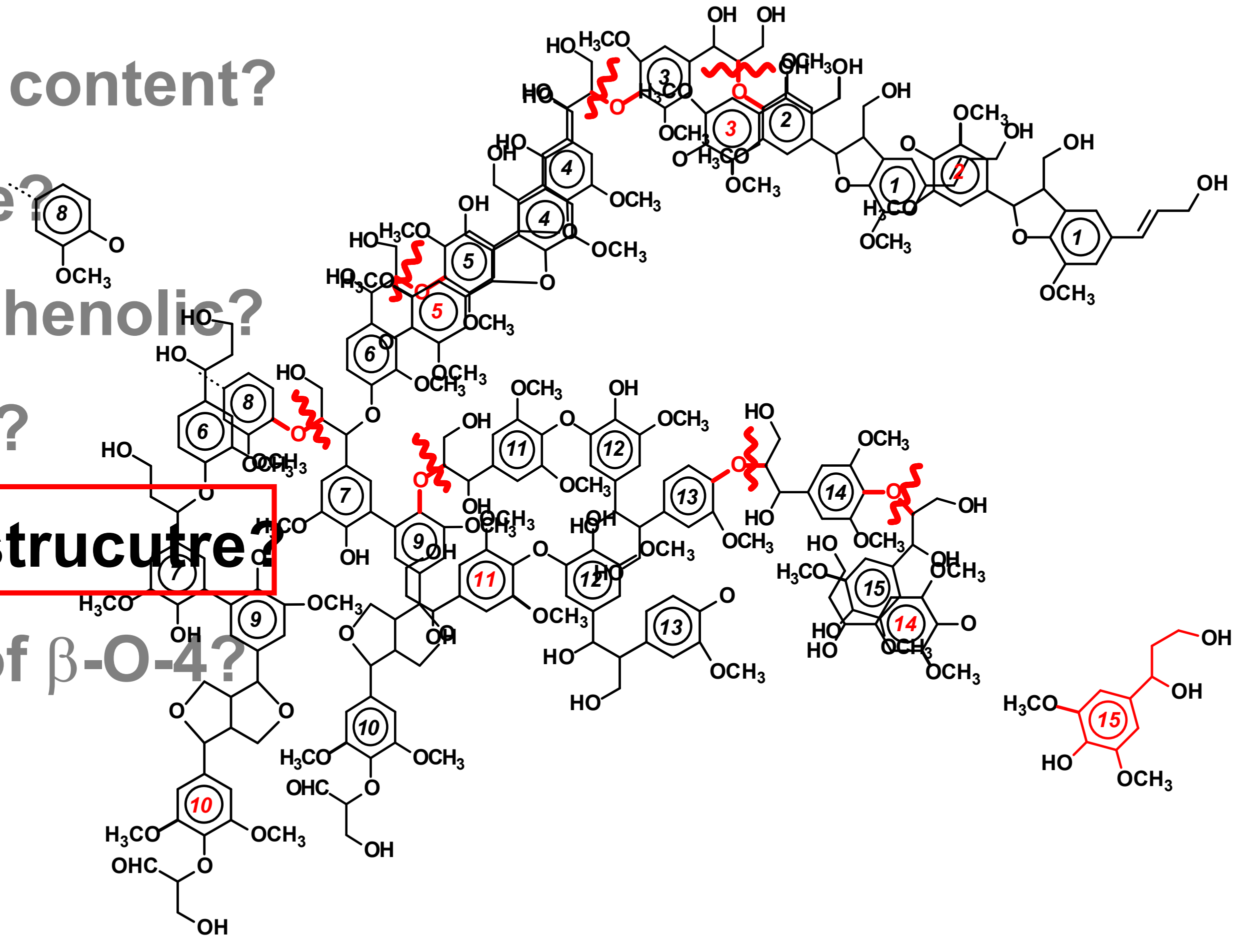
stereo structure of β-O-4?

etc



so many factors which could affect reactivity of lignin !

Wide variety of lignin structure and amount



low or high lignin content?

aromatic ring type?

phenolic or non-phenolic?

interunit linkages?

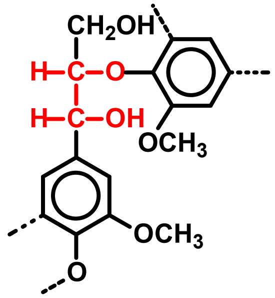
amount of β-O-4 strucutre?

stereo structure of β-O-4?

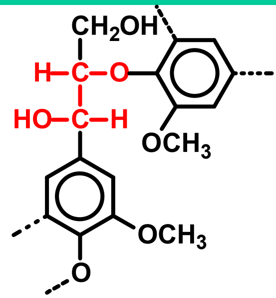
etc

so many factors which could affect reactivity of lignin !

Wide variety of lignin structure and amount



erythro β-O-4 structure



threo β-O-4 structure

low or high lignin content?

aromatic ring type?

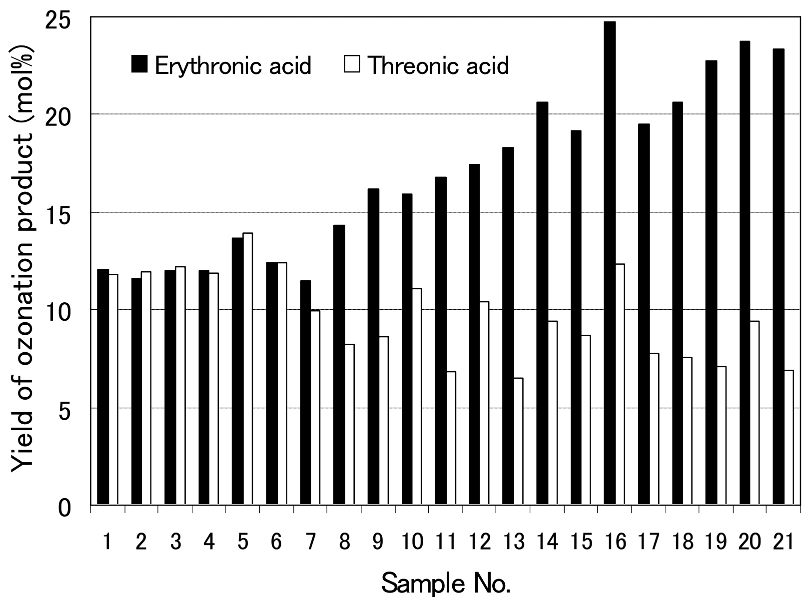
phenolic or non-phenolic?

interunit linkages?

amount of β-O-4 strucutre?

stereo structure of β-O-4?

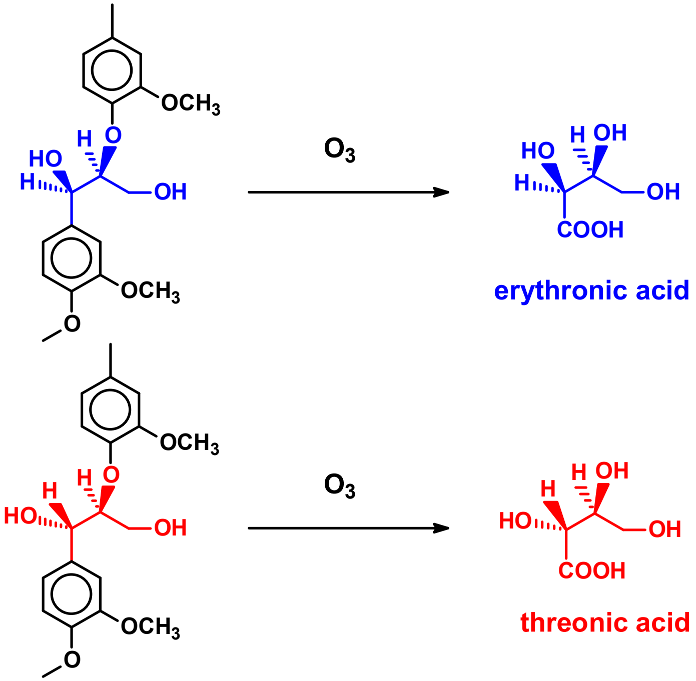
etc



E/T : 1 – 4.0

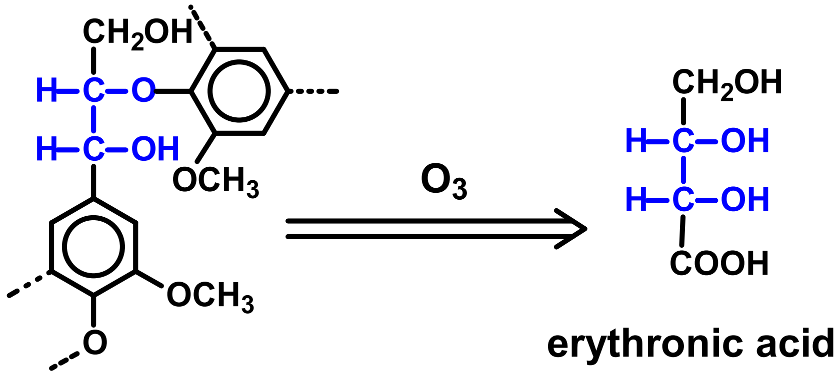
so many factors which could affect reactivity of lignin !

method to analyze stereo structure of β-O-4



erythronic acid

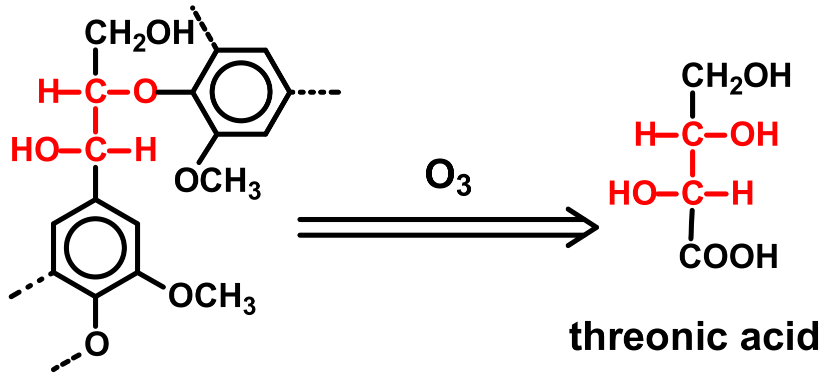
threonic acid



erythro β-O-4 structure

erythronic acid

E



threo β-O-4 structure

threonic acid

T

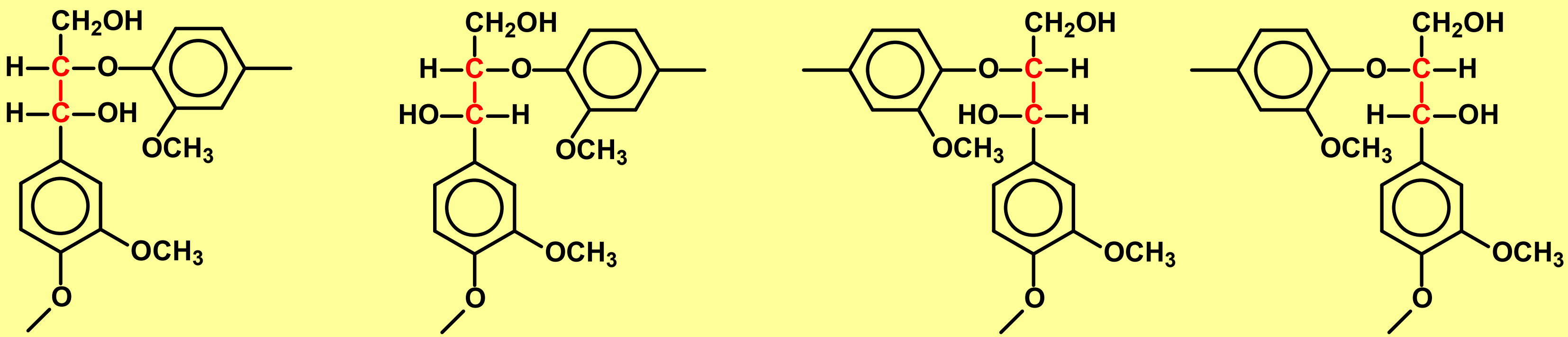
E ratio: E / (E+T)

E/T ratio: E / T

About the optical activity of lignin

Absolute configuration of β -O-4 structure in native lignin (Beech)

Fig G

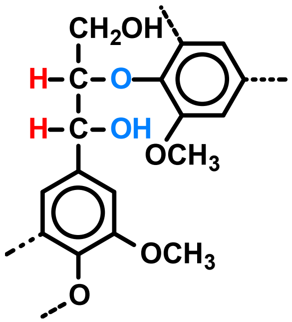


erythro	*threo*	*erythro*	*threo*
[α*R*, β*S*]	[α*S*, β*S*]	[α*S*, β*R*]	[α*R*, β*R*]
36 - 37%	12 - 13%	37 - 38%	13 - 14%

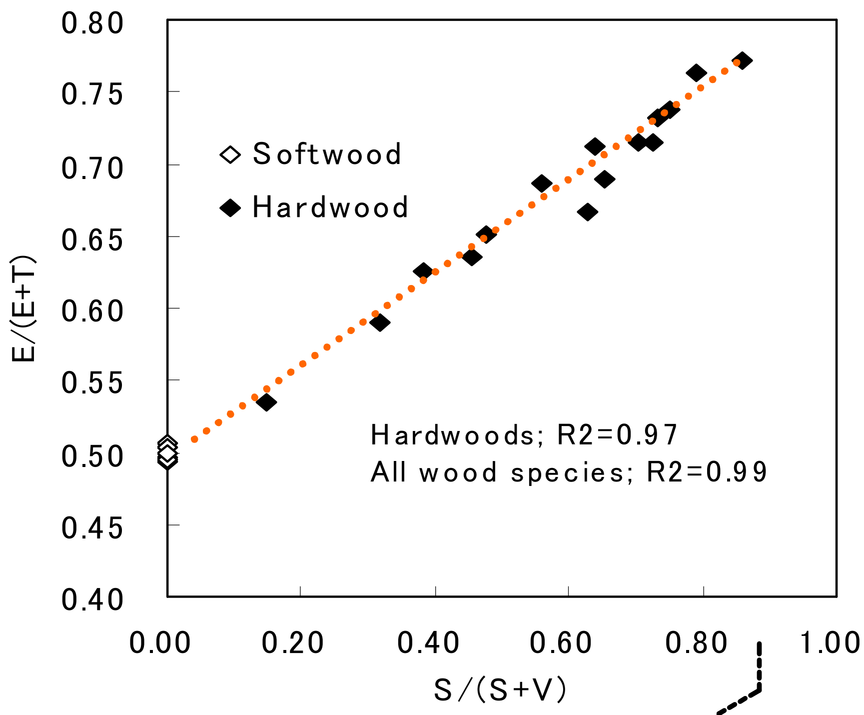
Japanese Beech (*Fagus crenata*) was subjected to ozonation analysis.
Ratio between *erythro* and *threo* form of β -O-4 structure was obtained to be 2.7 by measuring the ratio of erythronic acid and threonic acid in ozonation products.
By the comparison with authentic samples (D-erythronic acid and L-threonic acid), enantiomer excess of erythronic acid and threonic acid in ozonation products were determined. Any significant enantiomer excess was not detected both for erythronic acid and threonic acid. These lead to a conclusion that both erythro and threo b-O-4 structures are present as racemic forms.
Absolute configuration of α - and β - carbons of Beech β -O-4 structure are shown in **Figure G**.

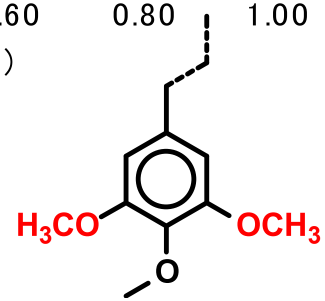
β-O-4 structure is present as racemic form in lignin !!

Role of the syringyl unit……



***erythro* β-O-4**





syringyl

It seems that the appearance of syringyl unit resulted in a simplification of lignin structure

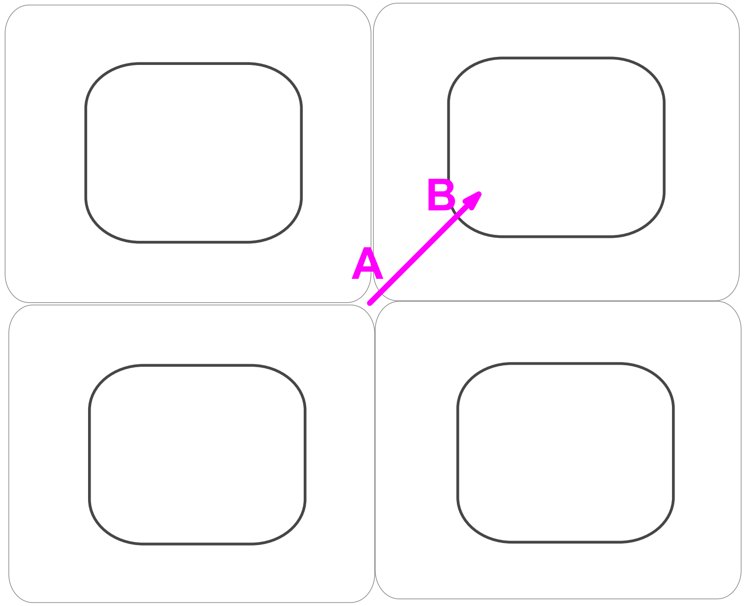
What is the rule when the nature create lignin in woody cell wall?

Akiyama et al: *Holzforschung*, 59(3), 276-281, 2005

Sample No.	Wood species		Harvest	Sampling
Softwood				
1	*Cedrus deodara*	Deodara Cedar	Japan, 2001	Sapwood
2	*Ginkgo biloba* [1]	Maidenhair Tree	Japan, 2001	Sapwood
3	*Abies sachalinensis*	Sachalin Fir	Japan	Sapwood
4	*Agathis loranthifolia*	Agathis	Indonesia	Stem
5	*Cryptomeria japonica*	Japanese Cedar	Japan, 2000	Sapwood
6	*Pinus densiflora*	Japanese Red Pine	Japan, 2001	Sapwood
Hardwood				
7	*Eusideroxylon zwageri*	Ulin	Indonesia	Stem
8	*Dalbergia latifolia*	Sonokeling (Blackwood)	Indonesia, 1999	Heartwood
9	*Acacia mangium*	Acacia mangium	Indonesia	Sapwood
10	*Plumeria alba*	White Frangipani	Indonesia, 2002	Sapwood
11	*Mimusops elengi*	Tanjung	Indonesia, 2002	Sapwood
12	*Celtis sinensis*	Japanese Hackberry	Japan, 2001	Sapwood
13	*Eucalyptus florencia*	Eucalyptus	Indonesia	Sapwood
14	*Melaleuca cajuputi*	Melaleuca	Thailand, 1996	Sapwood
15	*Hevea brasiliensis*	Para Rubber Tree	Thailand	Stem
16	*Firmiana simplex*	Chinese Parasol Tree	Japan, 2001	Sapwood
17	*Rhizophora sp.*	Rhizophora	Indonesia, 2002	Stem
18	*Betula maximowicziana*	Monarch Birch	Japan, 1998	Sapwood [2]
19	*Liriodendron tulipifera*	Yellow Poplar	US	Sapwood [3]
20	*Fagus crenata*	Japanese Beech	Japan, 2000	Sapwood
21	*Avicennia sp.*	Avicennia	Indonesia, 2002	Stem

Analysis of lignin from different portion of cell wall

cross section of cell wall



A → B

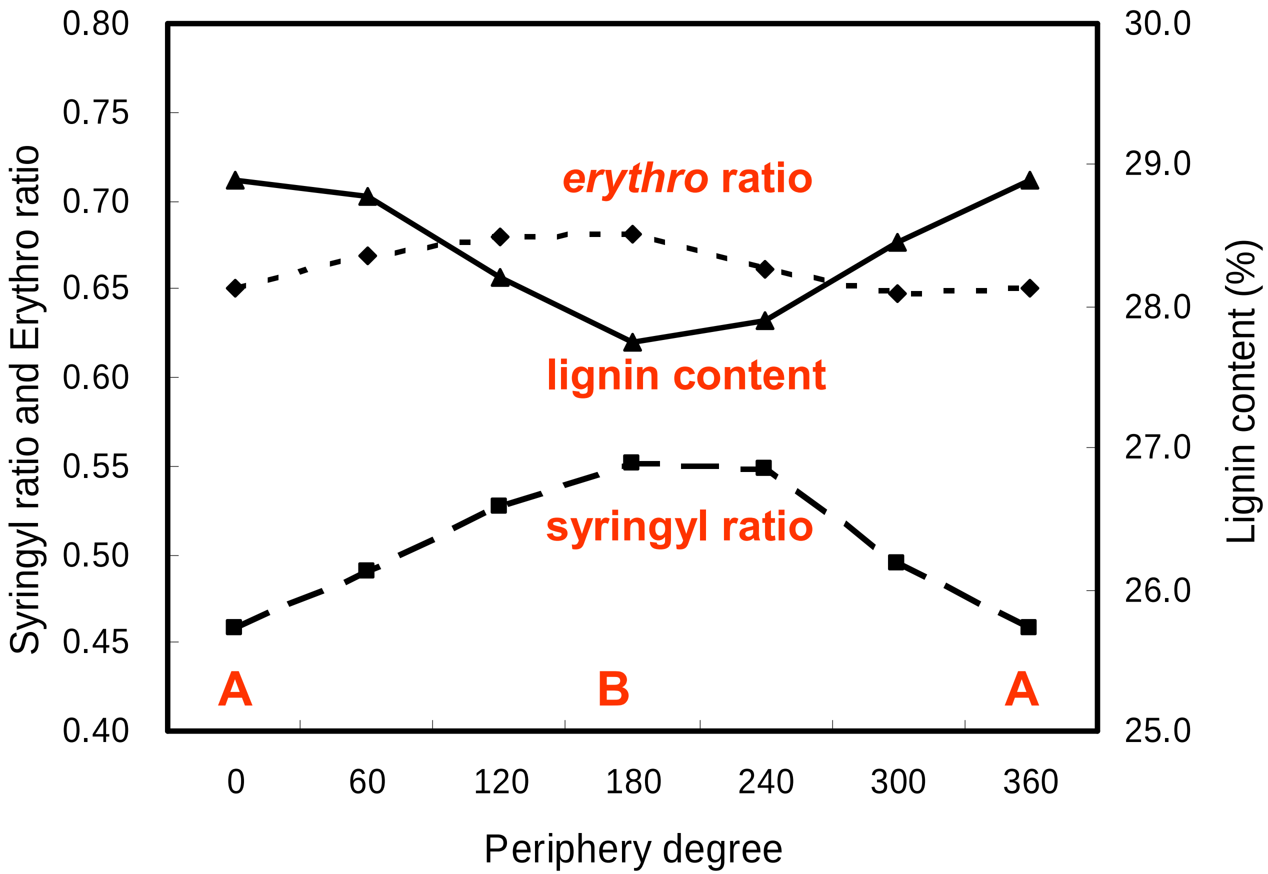
more lignin	less lignin
more guaiacyl	more syringyl
less ß-O-4	more ß-O-4
more condensed	less condensed
lower E/T ratio	higher E/T ratio

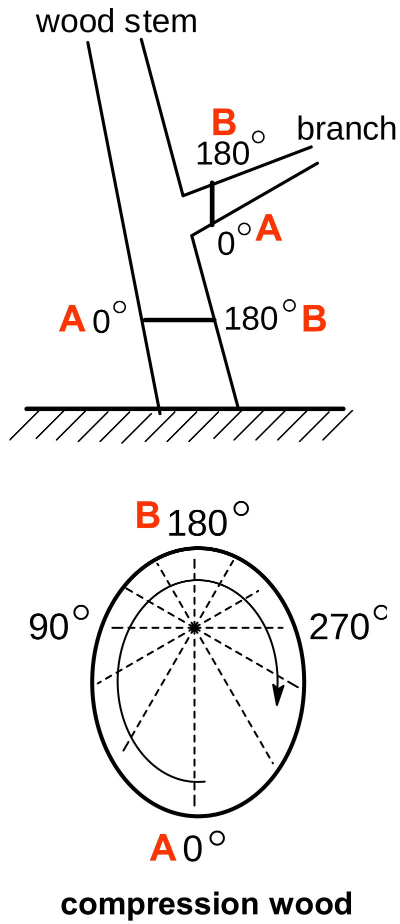
Method 1 Stepwise milling and extraction

Method 2 Direct sampling from developing xylem

Method 3 Analysis of wide variety of wood species and wood portions

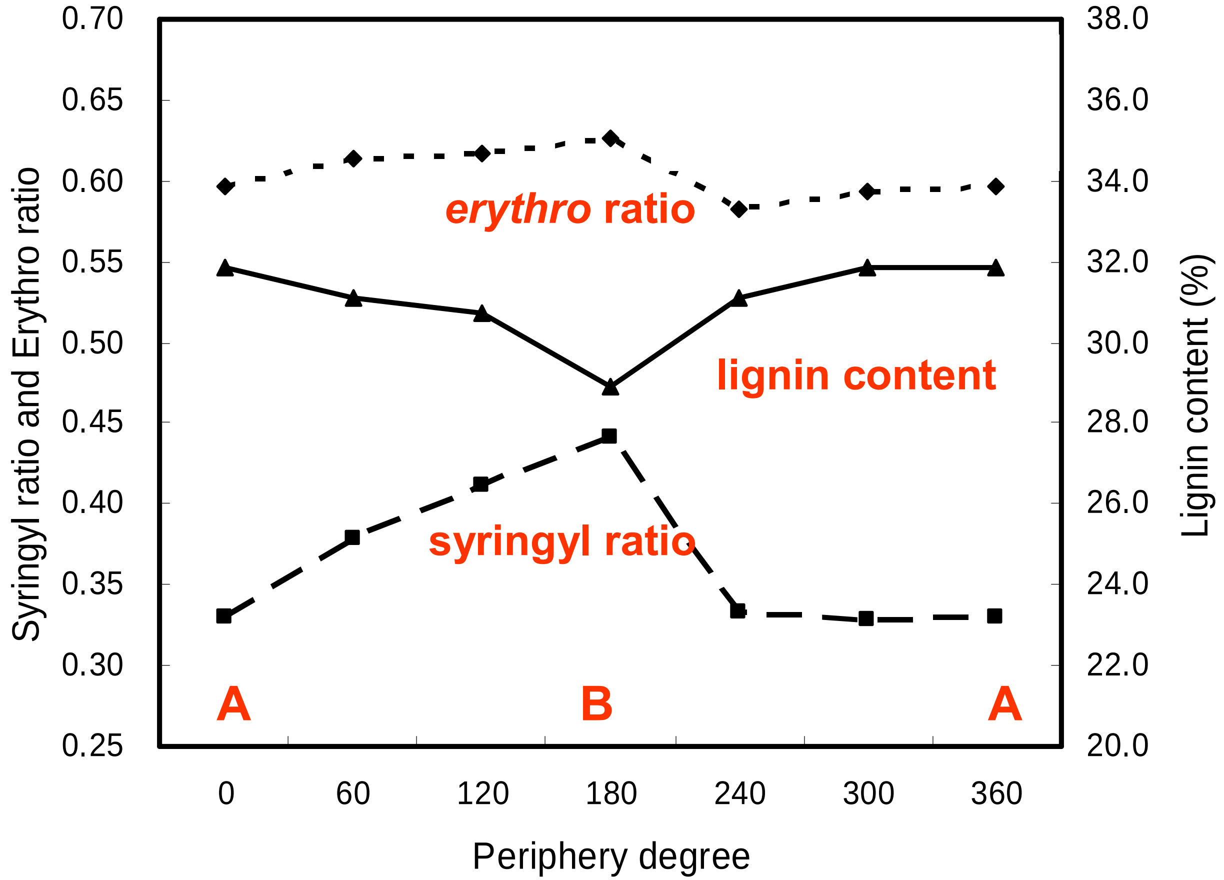
Compression wood with G-S type lignin

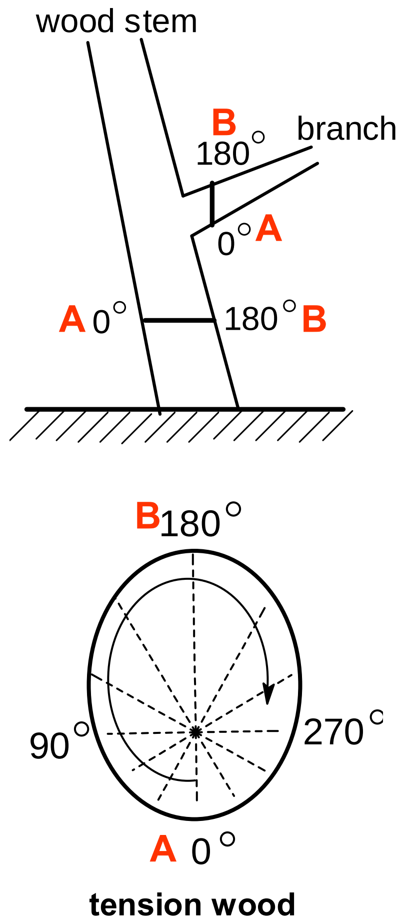




A	B
more lignin	less lignin
more guaiacyl	more syringyl
less ß-O-4	more ß-O-4
more condensed	less condensed
lower E/T ratio	higher E/T ratio

Typical tension wood with G-S type lignin





A	B
more lignin	less lignin
more guaiacyl	more syringyl
less ß-O-4	more ß-O-4
more condensed	less condensed
lower E/T ratio	higher E/T ratio

All these data can be summarized as following

lower S/V

more lignin

less β-O-4

lower *erythro/threo* ratio

more condensed

higher S/V

less lignin

more β-O-4

higher *erythro/threo* ratio

less condensed

Wood species examined (1) : Genus Acacia

Sample No.	Wood species	Country origin	Remarks
	Genus Acacia		
1	*Acacia auriculiformis*	Vietnam	
2	*Acacia hybrid*[*1]	Vietnam	Clone 1
3	*Acacia hybrid*[*1]	Vietnam	Clone 2
4	*Acacia hybrid*[*1]	Vietnam	Clone 3
5	*Acacia hybrid*[*1]	Vietnam	Clone 4
6	*Acacia hybrid*[*1]	Vietnam	Clone 5
7	*Acacia hybrid*[*1]	Vietnam	Clone 6
8	*Acacia mangium*	Indonesia	
9	*Acacia mangium*[*2]	Malaysia	P-1
10	*Acacia mangium*[*2]	Malaysia	P-2; 8 years old
11	*Acacia mangium*[*2]	Malaysia	P-2; 12 years old
12	*Acacia mangium*[*2]	Malaysia	P-3
13	*Acacia mangium*[*2]	Malaysia	P-4
14	*Acacia mangium*	Papua New Guinea	
15	*Acacia meransii*	South Africa	

*1: Hybrid of *Acacia mangium* and *auriculiformis* with different mother trees.

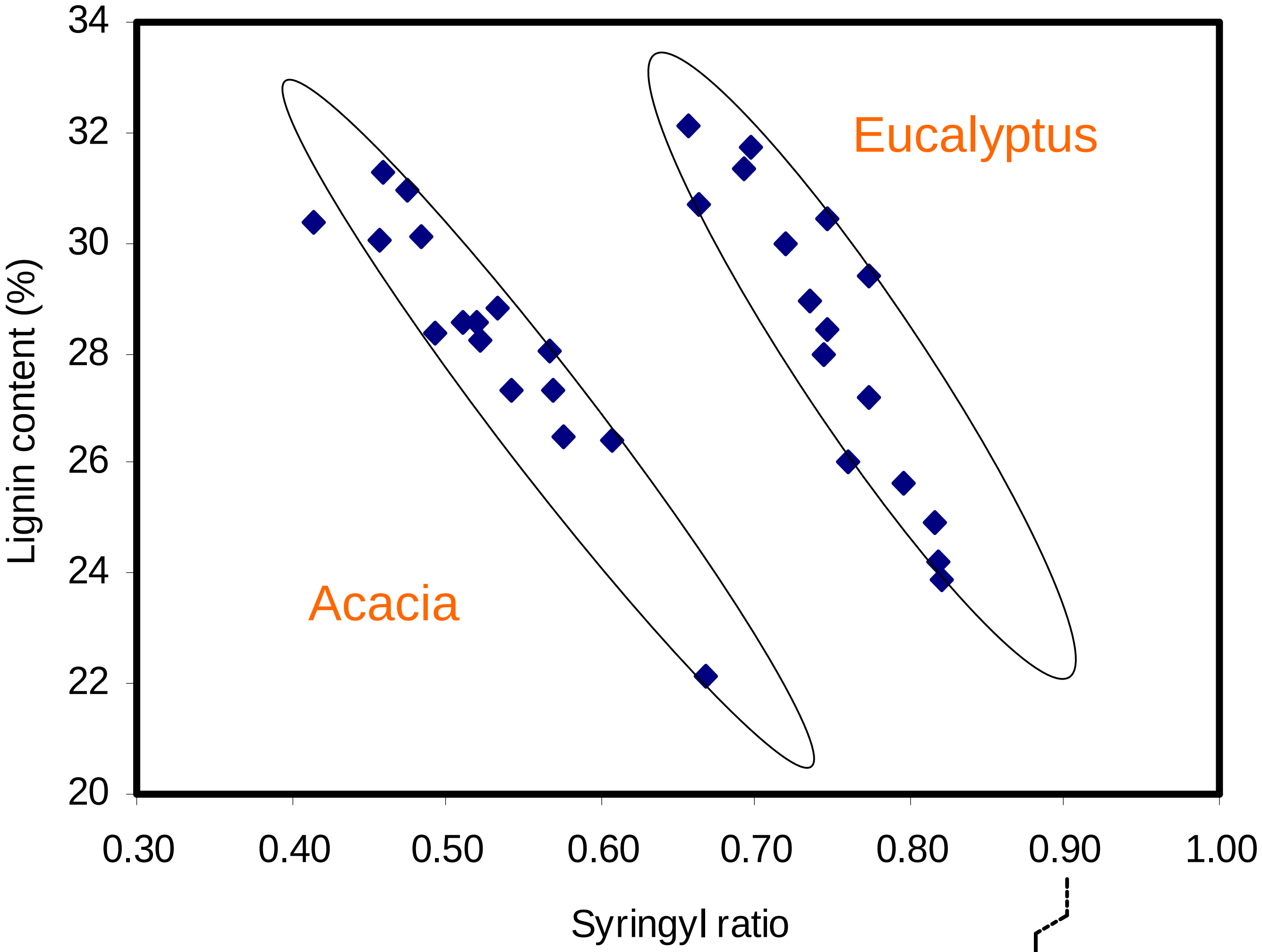
*2: P-1 to P-4 were taken from different plantation area in Malaysia.

Wood species examined (2) : Genus eucalyptus

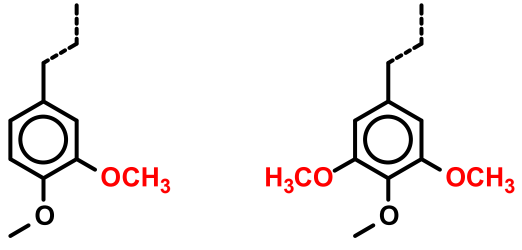
Sample No.	Wood species	Country origin	Remarks
	Genus Eucalyptus		
16	*Eucalyptus camaldulensis*	Thailand	
17	*Eucalyptus camaldulensis*	Vietnam	
18	*Eucalyptus deglupta*	Papua New Guinea	
19	*Eucalyptus dunii*	Australia	
20	*Eucalyptus globulus*	Australia	
21	*Eucalyptus globulus*	Chile	
22	*Eucalyptus grandis*	South Africa	P-1
23	*Eucalyptus grandis*	South Africa	P-2
24	*Eucalyptus grandis*	USA	
25	*Eucalyptus hybrid*[*3]	Laos	
26	*Eucalyptus nitens*	Australia	
27	*Eucalyptus saligna*	Africa	
28	*Eucalyptus urophylla*	Vietnam	

*3: Hybrid of *Eucalyptus camaldulensis* and *deglupta*

Syringyl ratio *vs* Lignin content

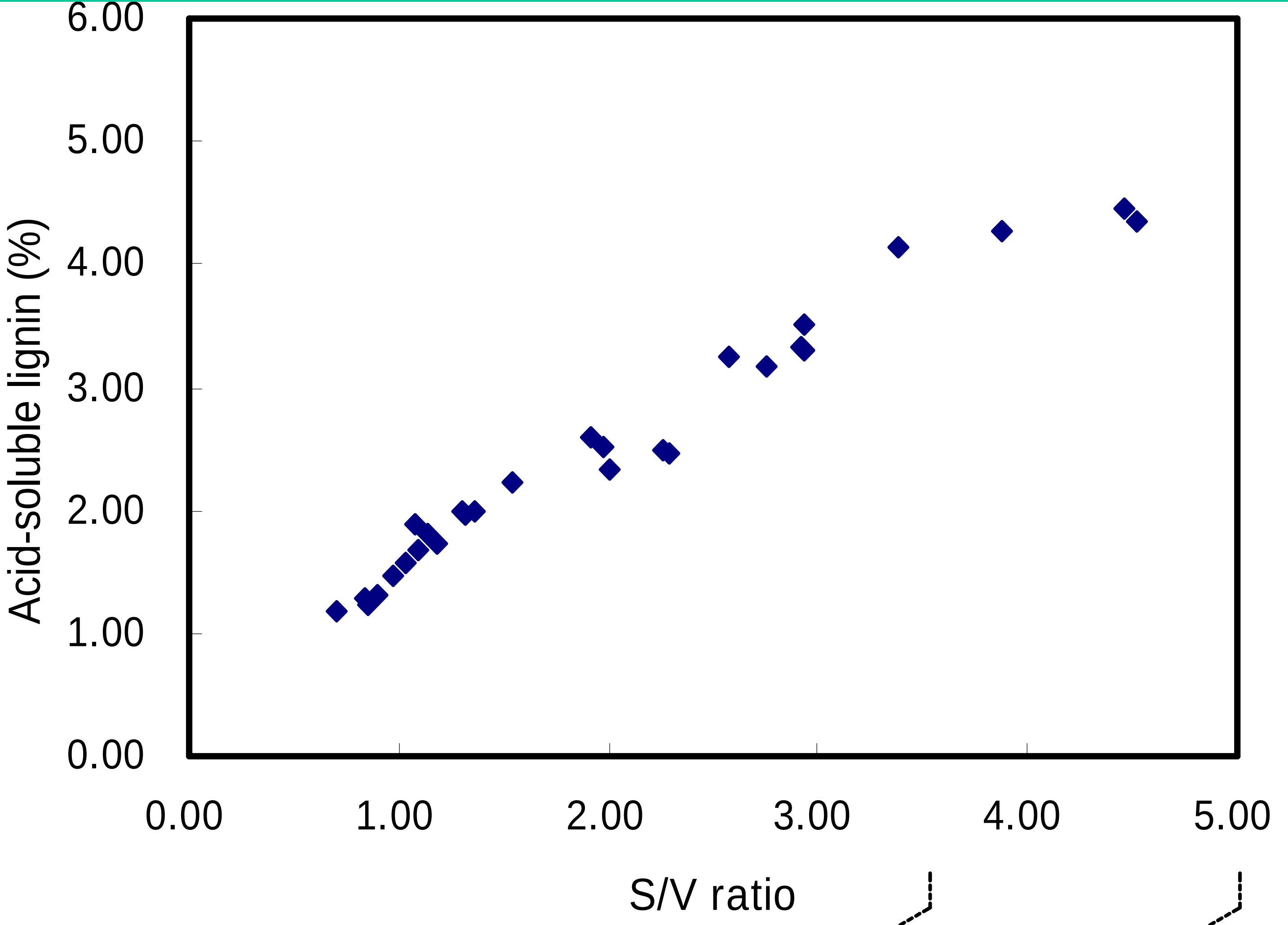


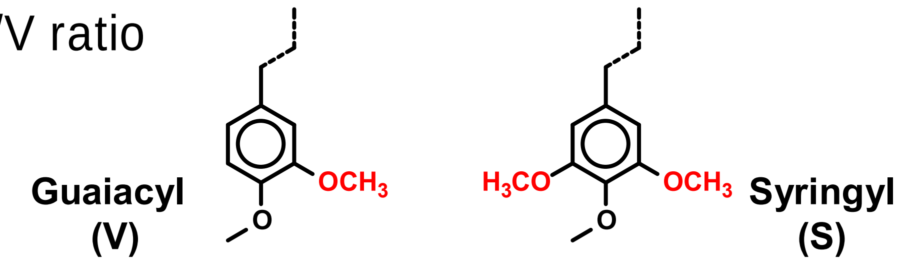
Guaiacyl (V)



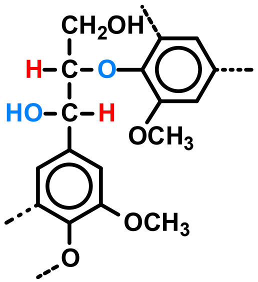
Syringyl (S)

Syringyl ratio vs acid soluble lignin (content)

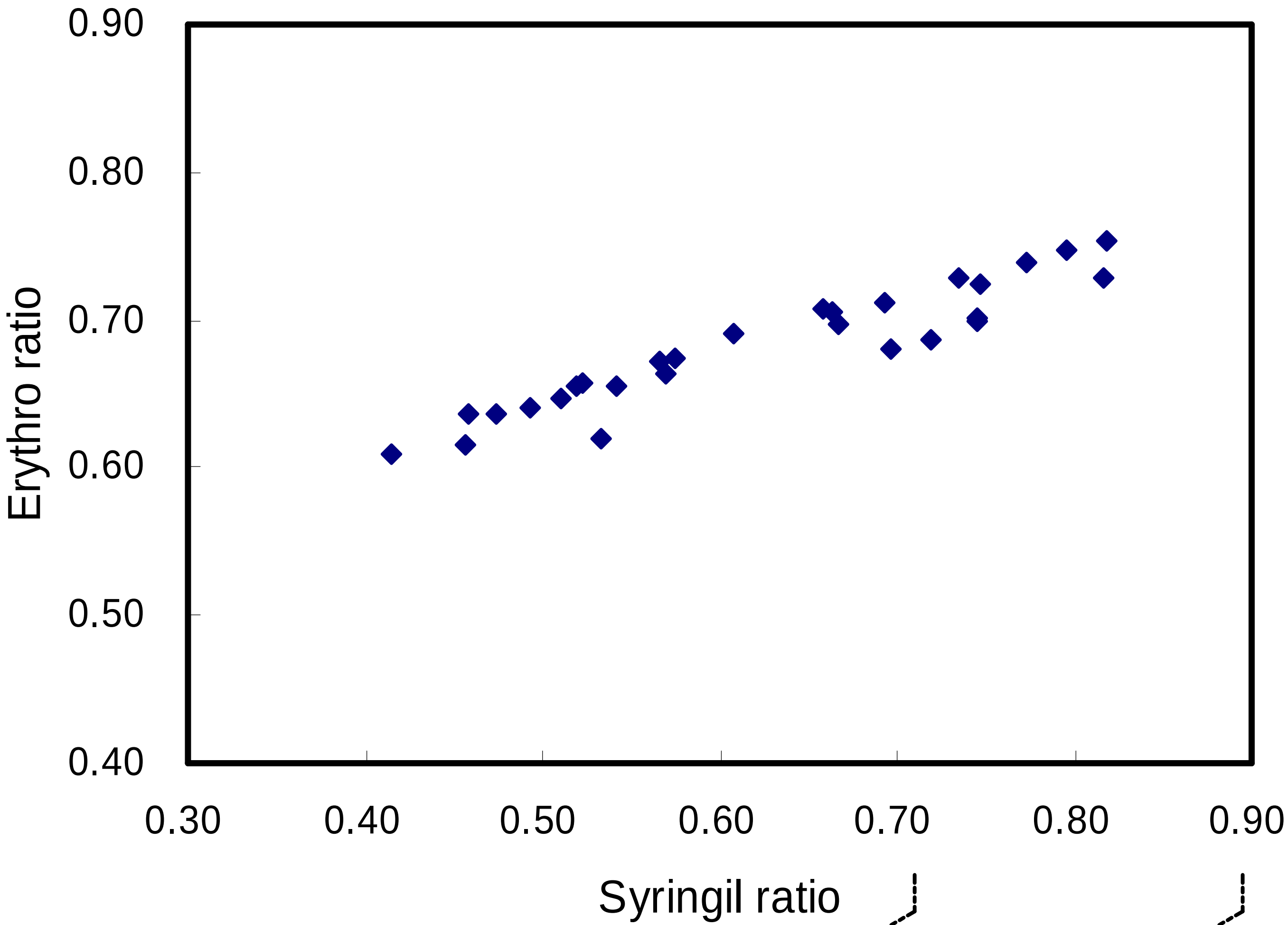




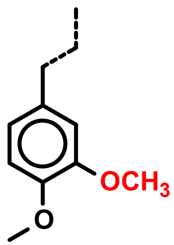
Syringyl ratio *vs* erythro ratio

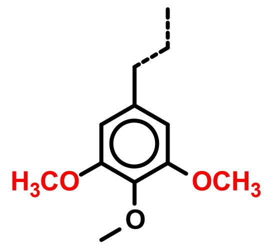


***threo* β-O-4**
(T)



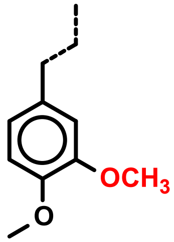
Guaiacyl
(V)



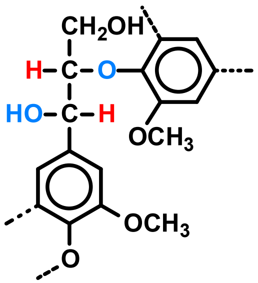


Syringyl
(S)

This is the “rule” when the nature creates lignin.

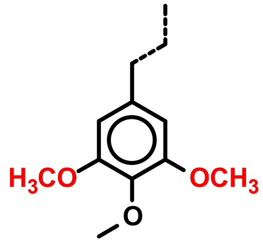


Guaiacyl
(V)

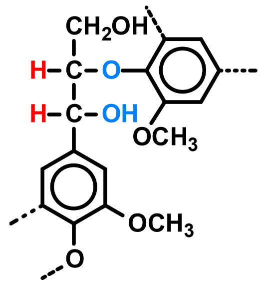


threo β-O-4
(T)

lower S/V	higher S/V
more lignin	less lignin
less β-O-4	more β-O-4
lower E/T ratio	higher E/T ratio
more condensed	less condensed



Syringyl
(S)



erythro β-O-4
(E)

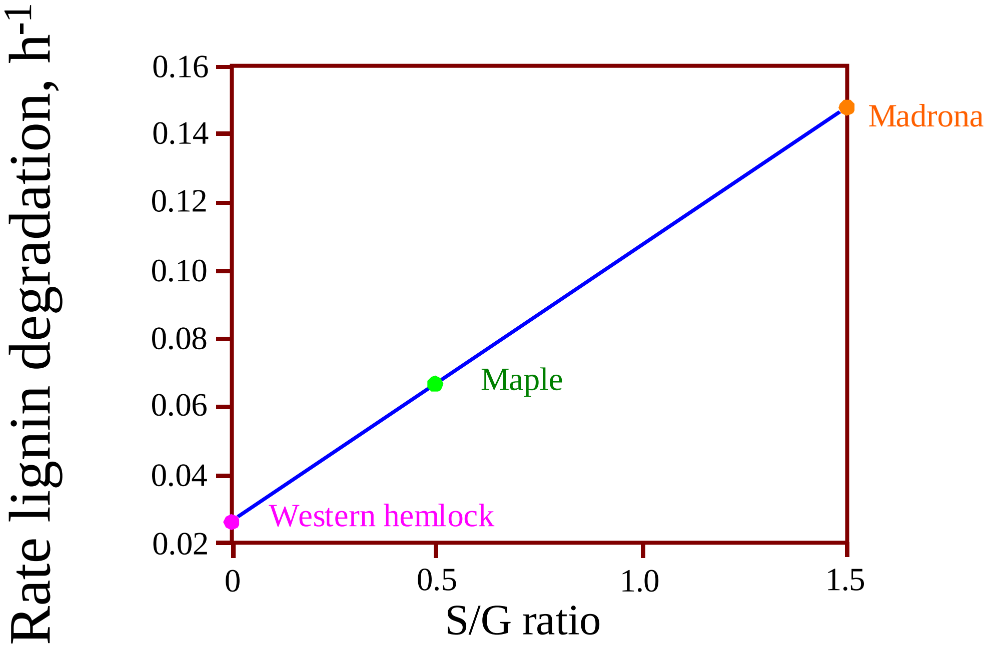
within a single cell wall (middle lamella → secondary wall)

within a single tree (1)
among different type of cell (vessel → fiber cell)

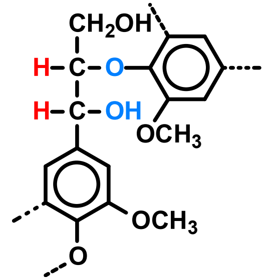
within a single tree (2) -------reaction wood
among different portion (compression site → tension site)

within the same wood species

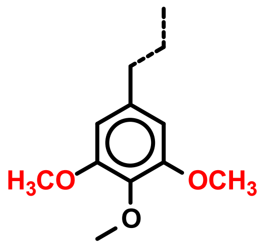
among variety of wood species



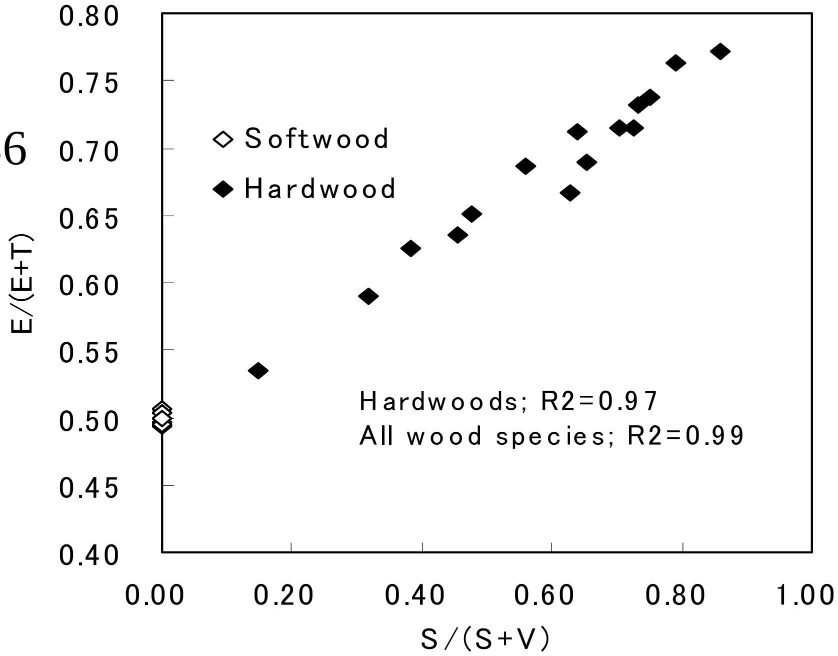
Chang and Sarkanen, 1973, *TAPPI*, 56: 132-136



erythro **β-O-4**
(E)

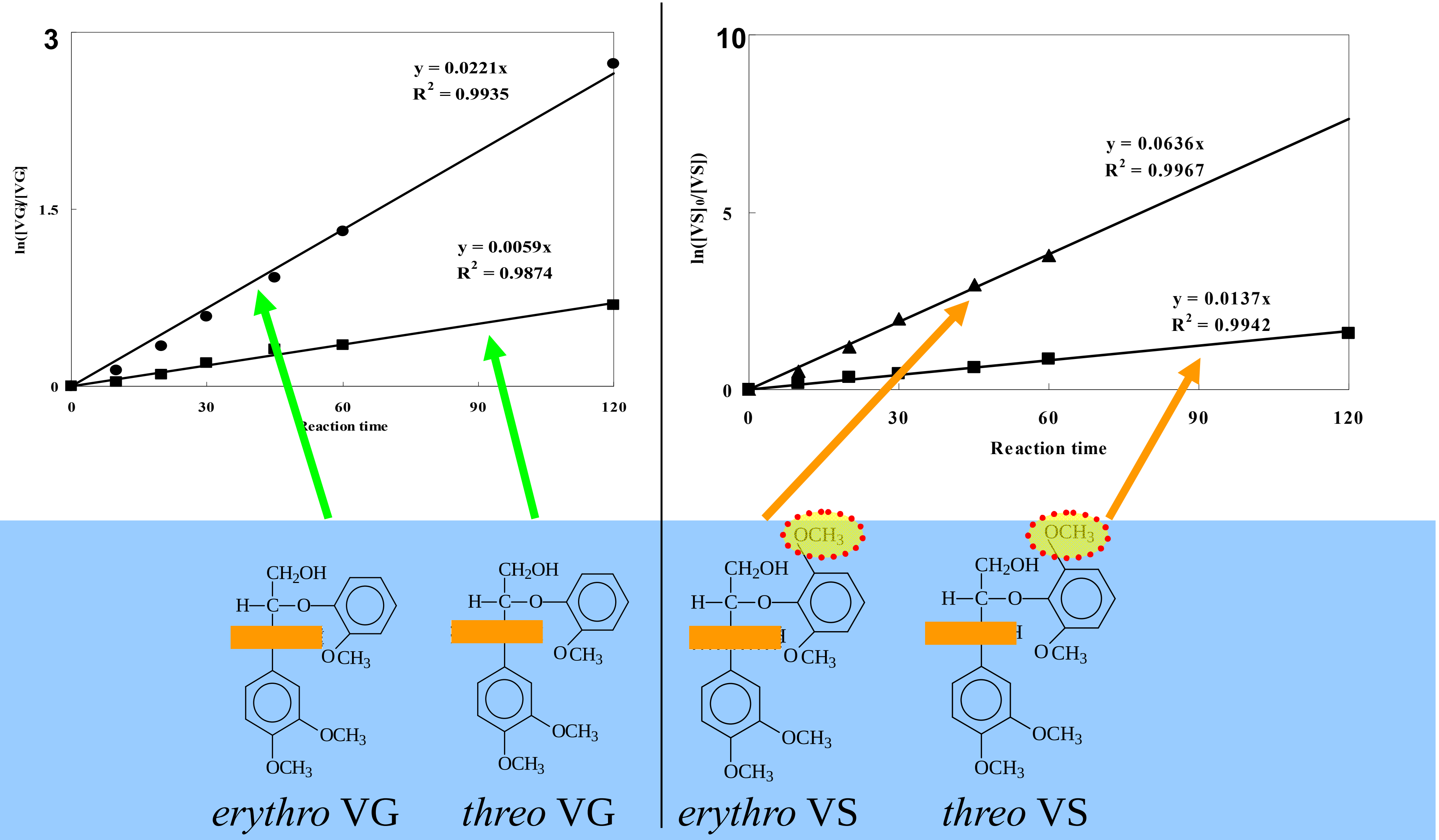


Syringyl
(S)



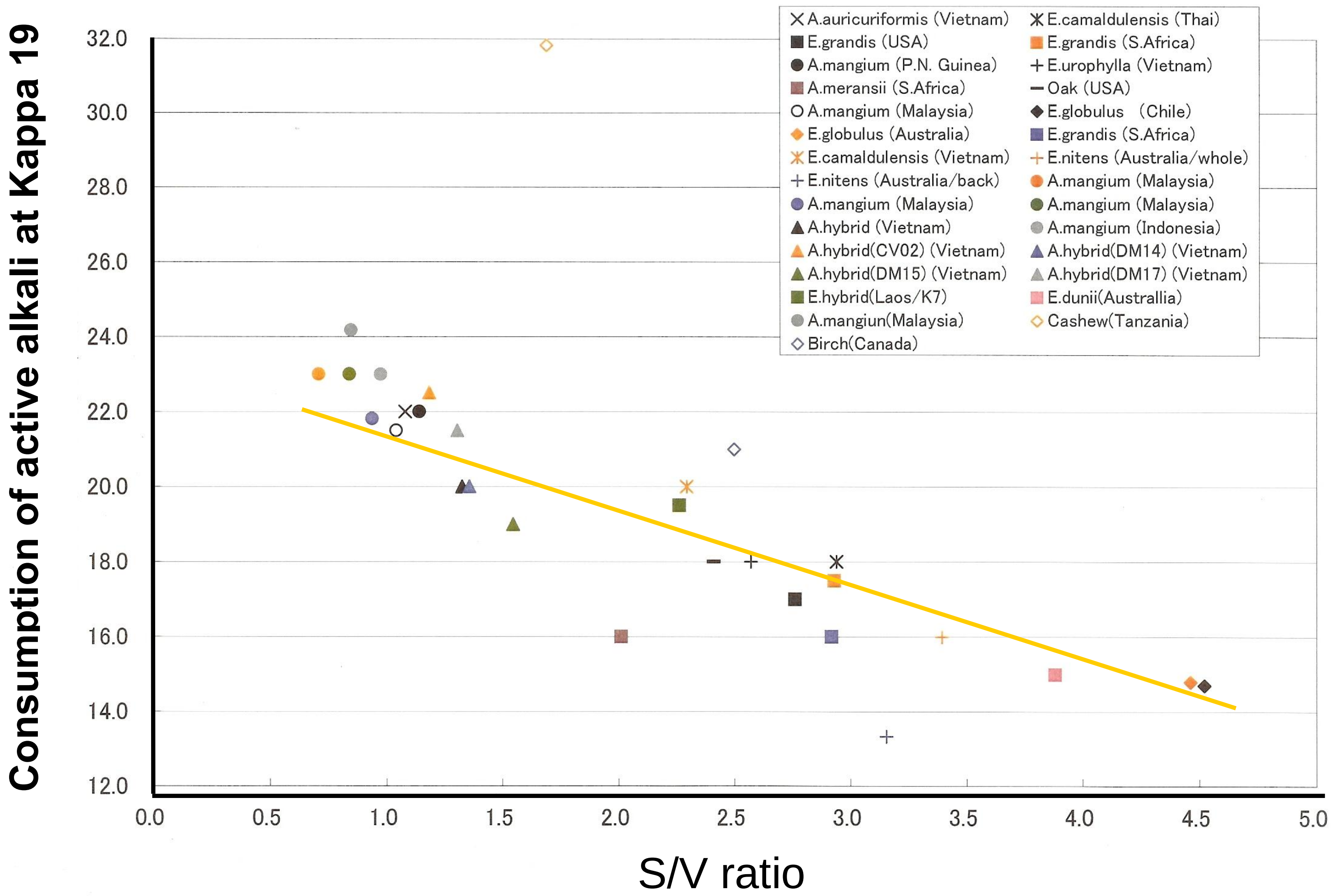
Akiyama, Matsumoto, 2005 , *Holzforschung*, 59, 276-281

What can be expected for the reactivity of β-O-4?



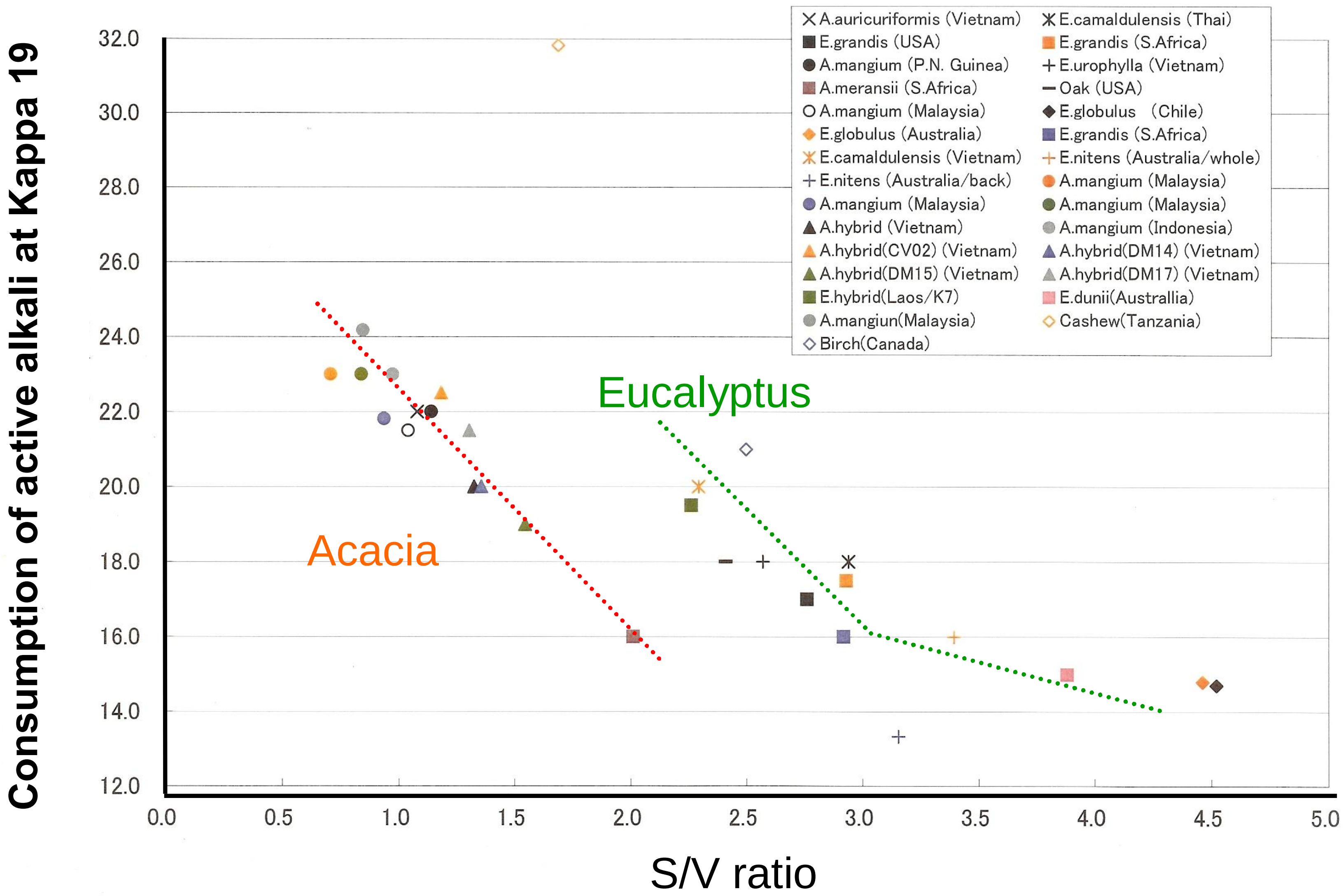
erythro faster than threo, syringyl faster than guaiacyl

S/V ratio *vs* pulpability (acacias and eucalyptus)



Cooperative research with Oji Paper Company

S/V ratio *vs* pulpability (acacias and eucalyptus)



Cooperative research with Oji Paper Company

Conclusion

Based on the analysis of genus acacia and eucalyptus

lower S/V	higher S/V
more lignin	less lignin
less β-O-4	more β-O-4
lower *E/T* ratio	higher *E/T* atio
more condensed	less condensed
worse reactivity	better reactivity

Structure of hemicellulose?

Thank you very much!!