Thermal characterization of lignins

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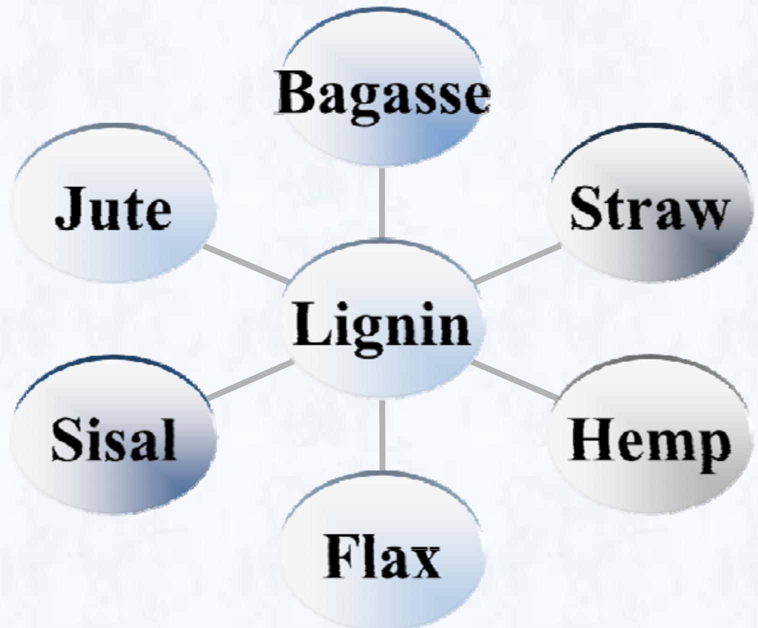
Aim

To compare the thermal behavior of lignins from different fiber crops and to find a correlation between thermal characteristics of the phase transition and degradation temperatures.

Materials



Methods

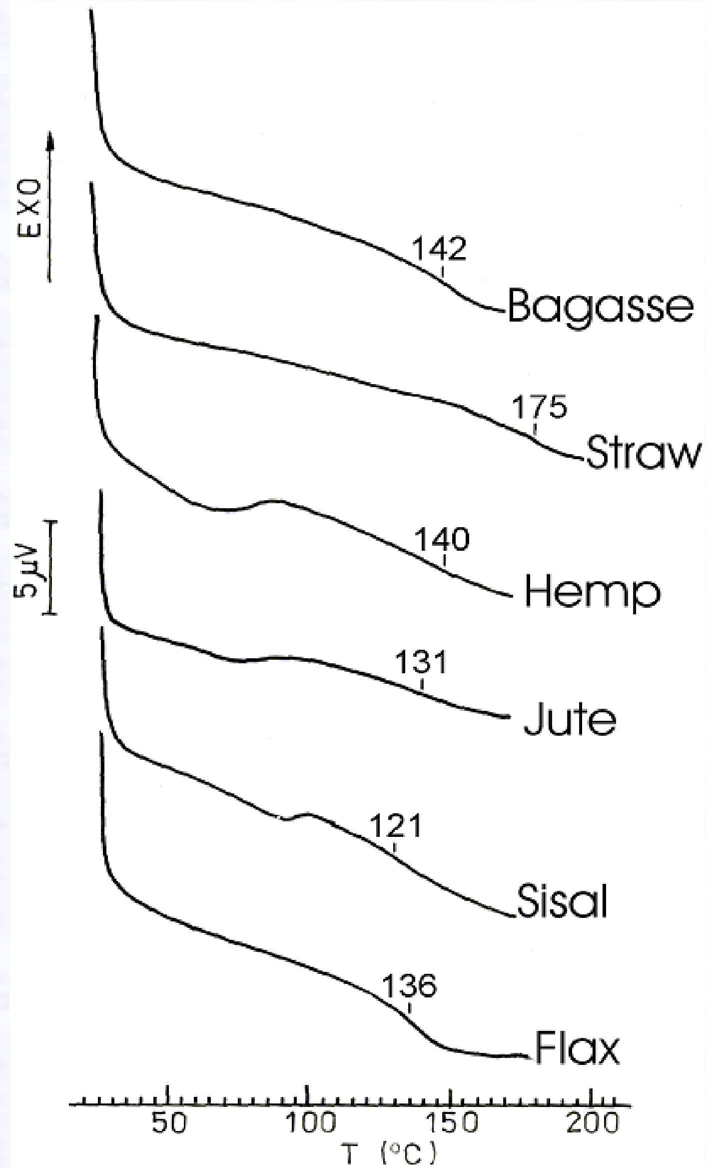
Differential scanning calorimetry
Thermogravimetry
FT-IR spectroscopy
2D IR correlation spectroscopy

DSC curves

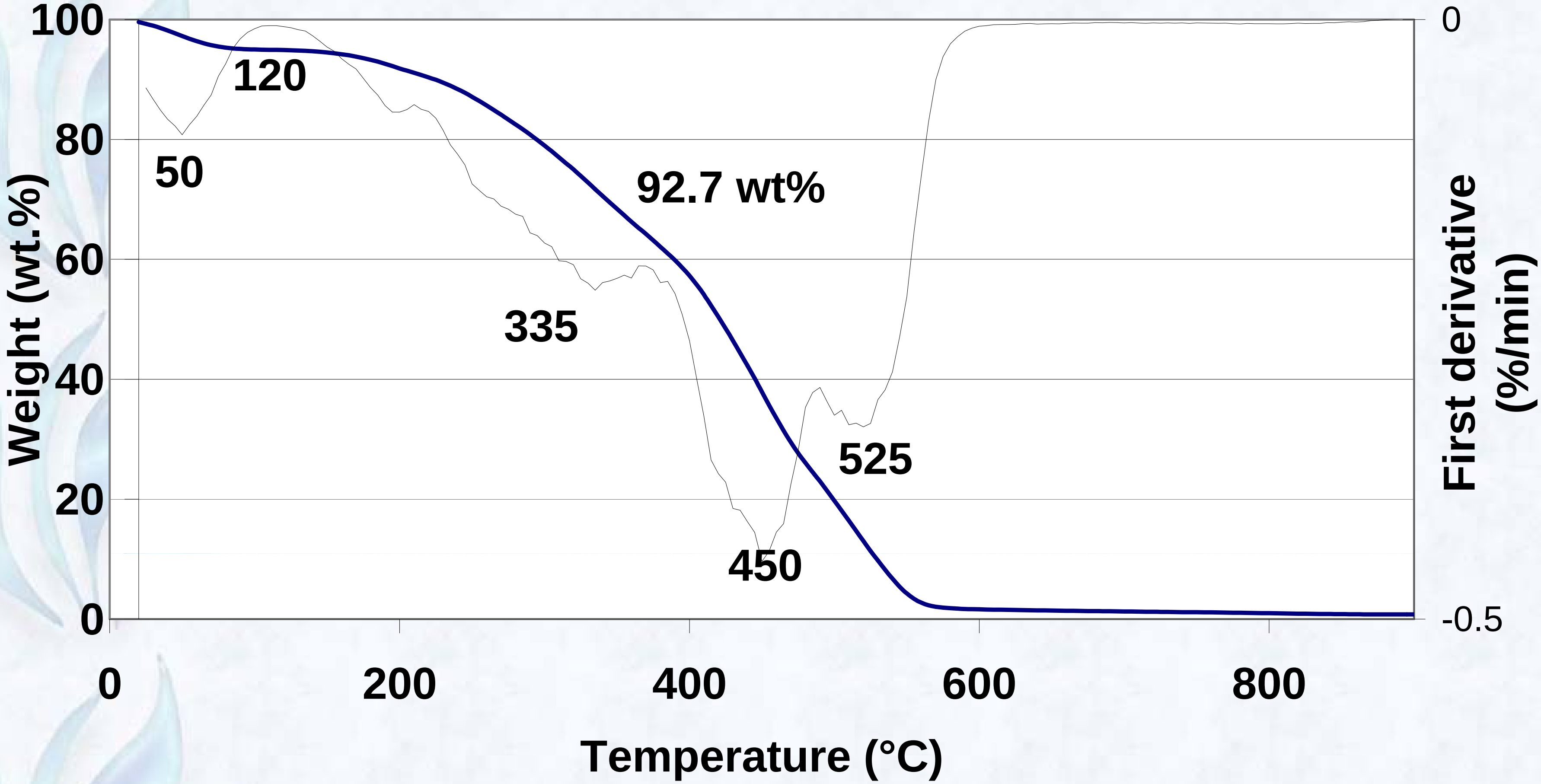
Lignin is an amorphous polymer and undergo changes in physical characteristics on heating resulting in transitions to a glassy and rubbery state.

The temperature where this happens is referred to as the glass transition temperature or Tg.

The Tg of lignin is affected by such factors as the presence of low molecular weight contaminants (including water and solvents), molecular weight, thermal history, crosslinking, etc.



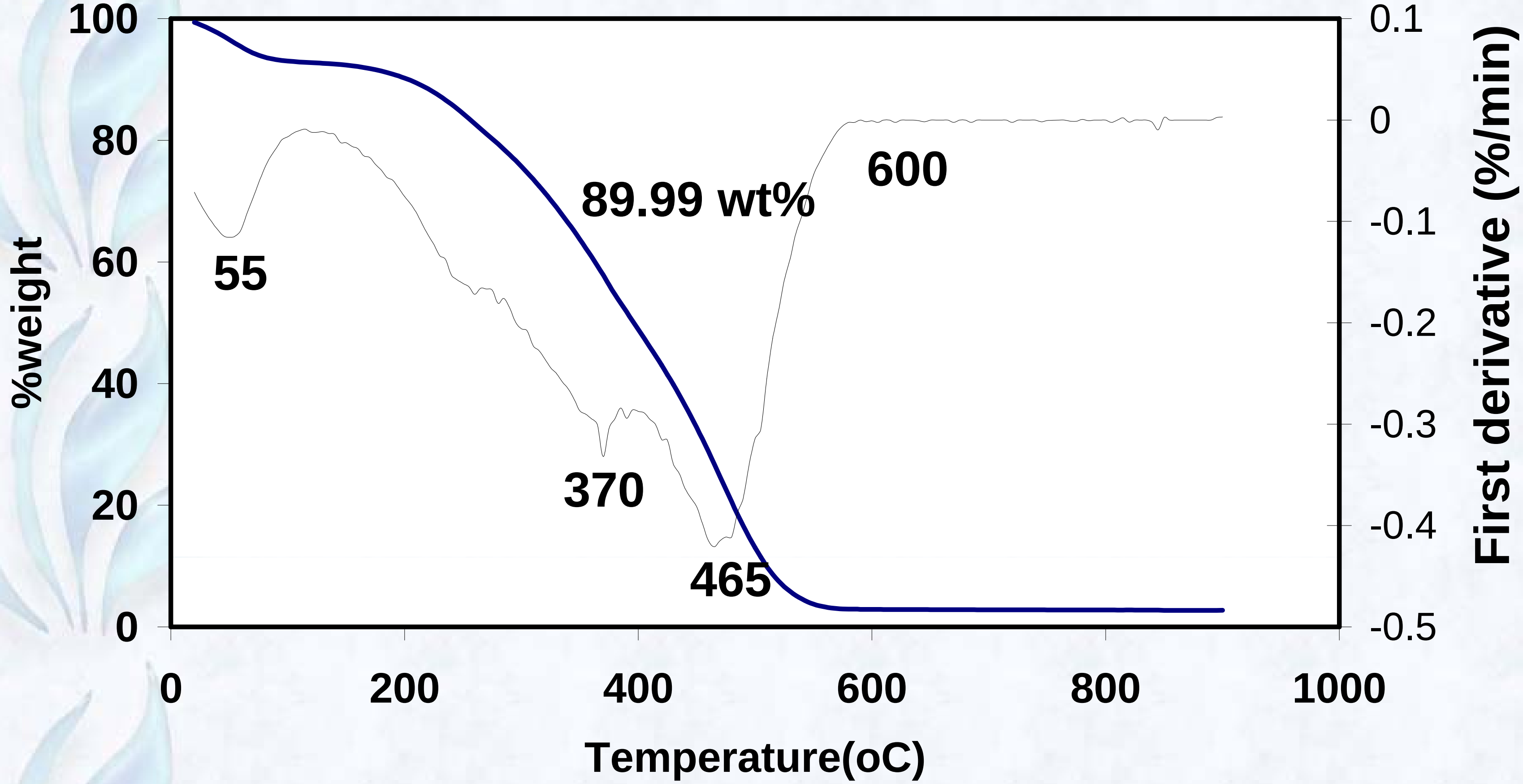
TG/DTG curves



Bagasse lignin shows a complex decomposition process resulted from 3 overlapped steps with the main maximum of mass loss rate at 335, 450 and 525 ^{o}C.

Total mass loss is 92.7 wt%

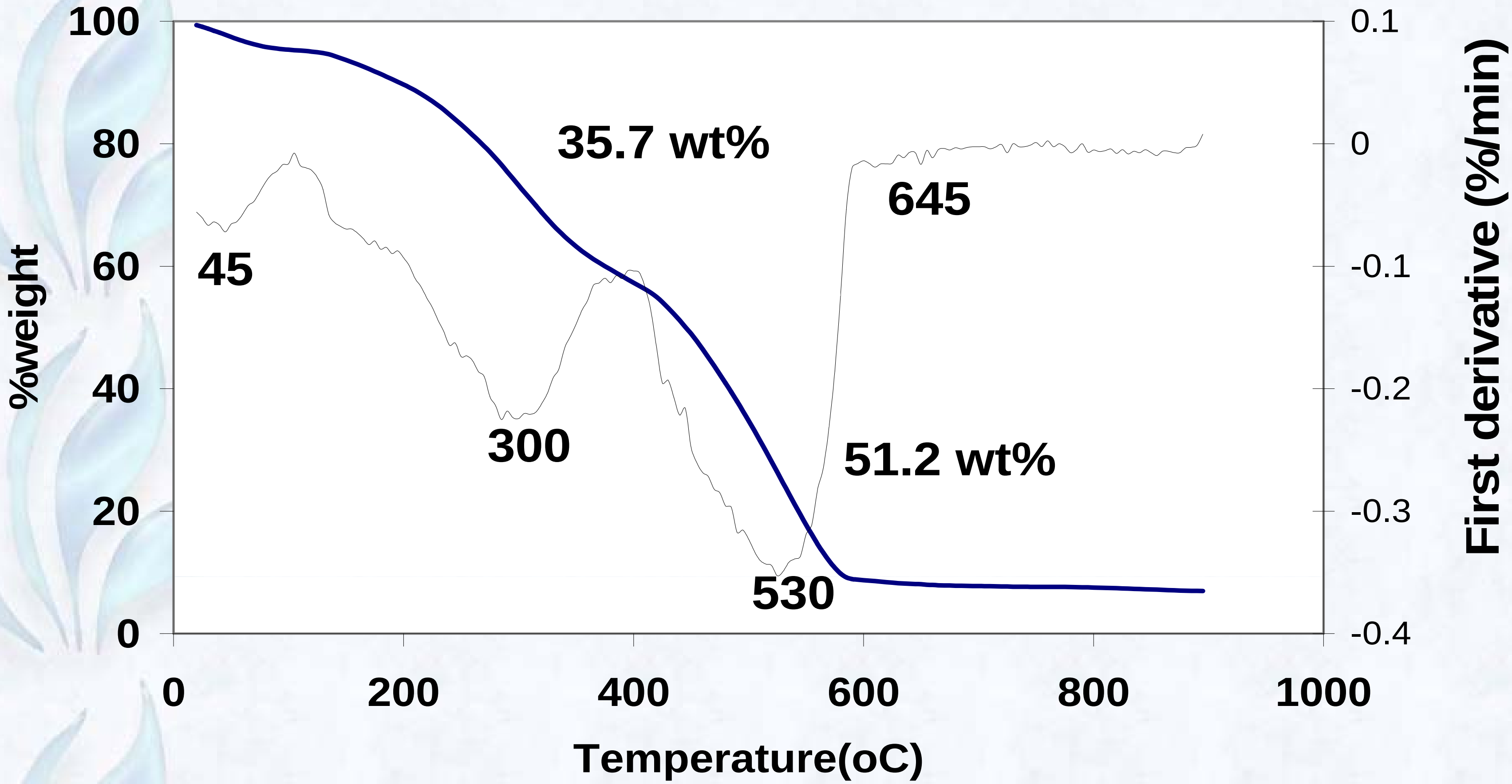
TG/DTG curves



Straw lignin decomposes in at least three overlapped processes with peak temperatures of ~240, 370 and 465 ^{o}C.

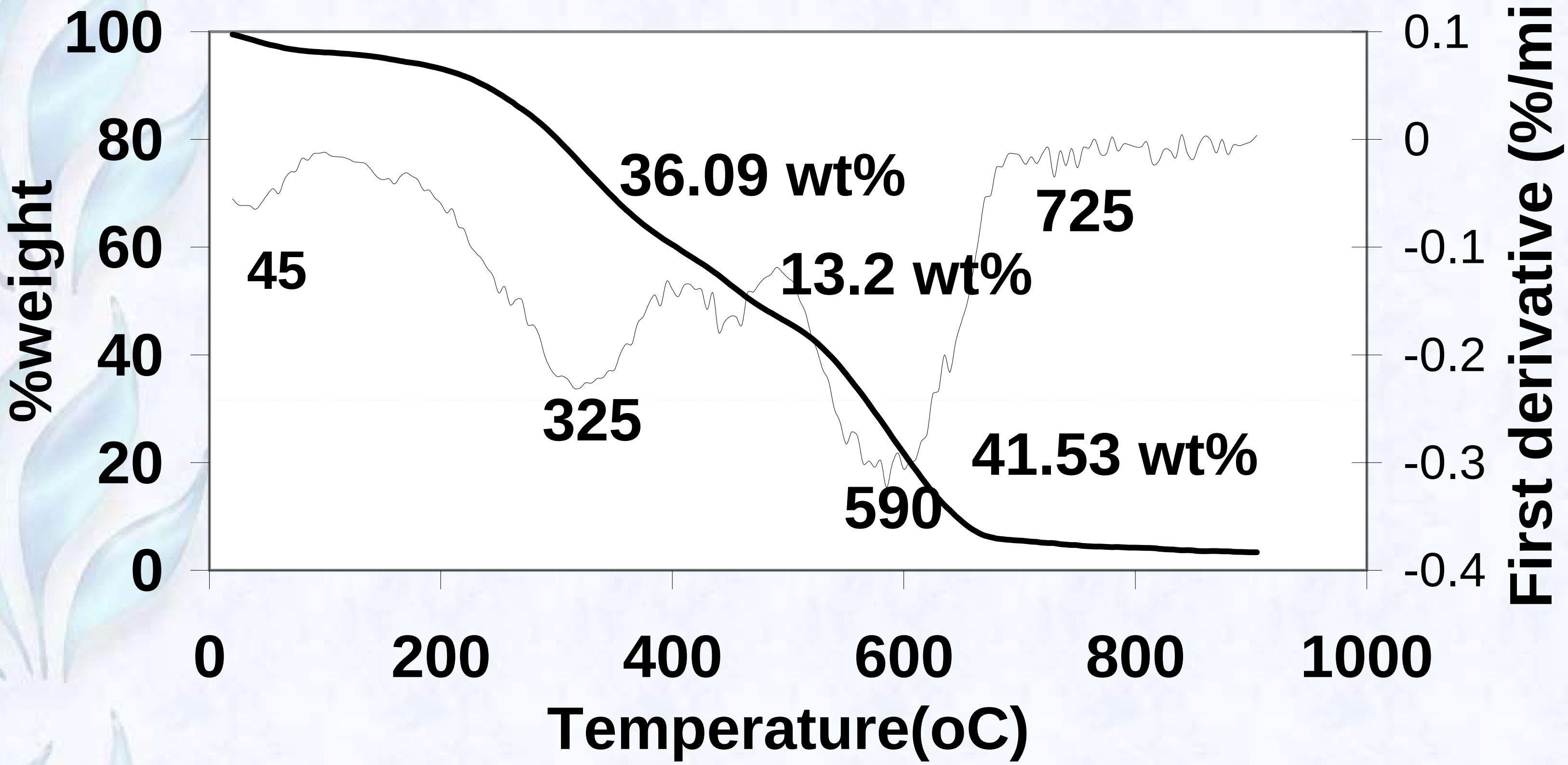
The total mass loss is of 89.99 wt%

TG/DTG curves



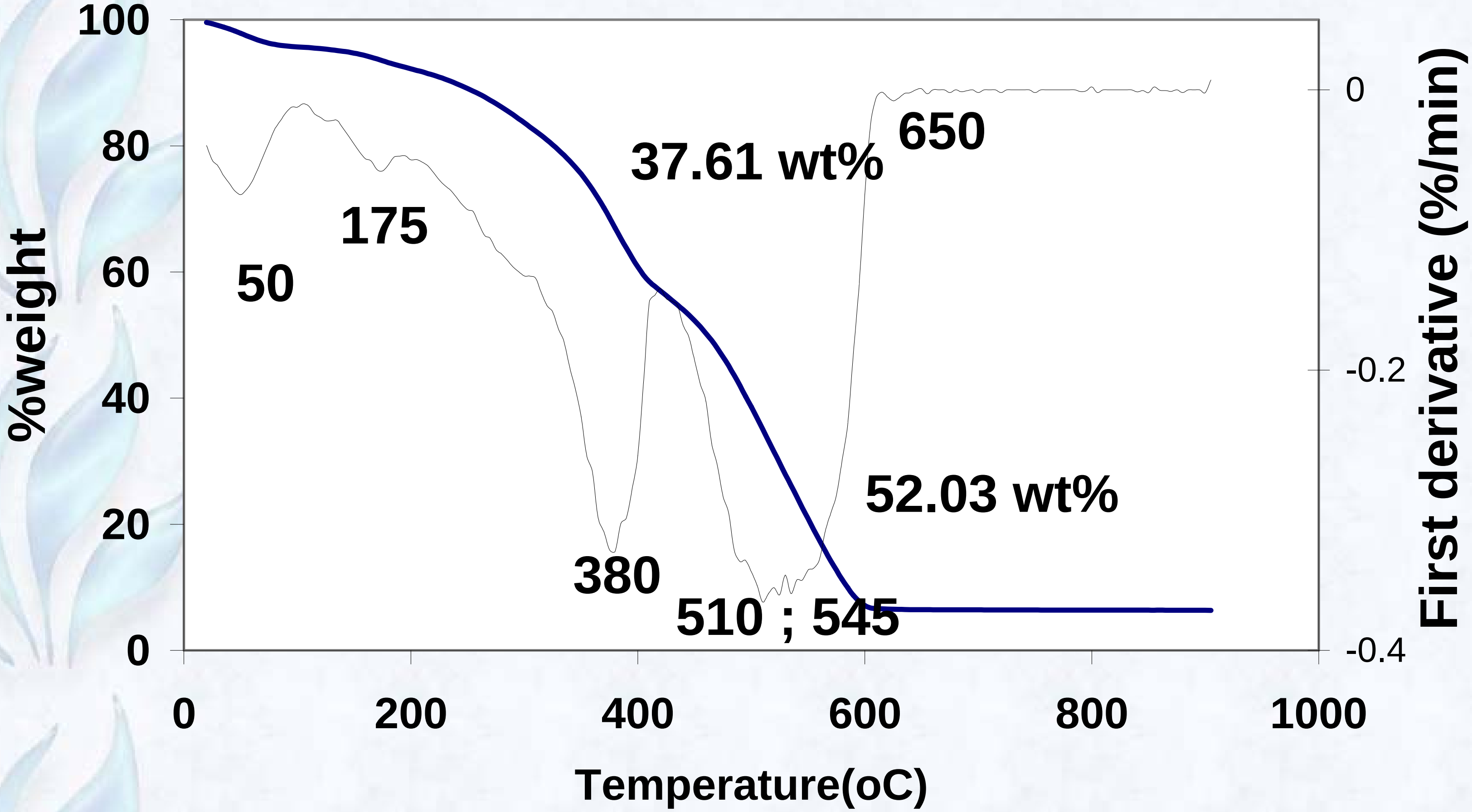
Hemp lignin decomposes in two steps relatively simple occurring in two different temperature regions. The peak temperatures are of 300 and 530 ^{o}C, the total mass loss is of 86.9 wt%.

TG/DTG curves



Flax lignin shows three overlapped steps. The peak temperatures are 325, 443 and 590 ^{o}C. The total mass loss is of 90.82 wt%.

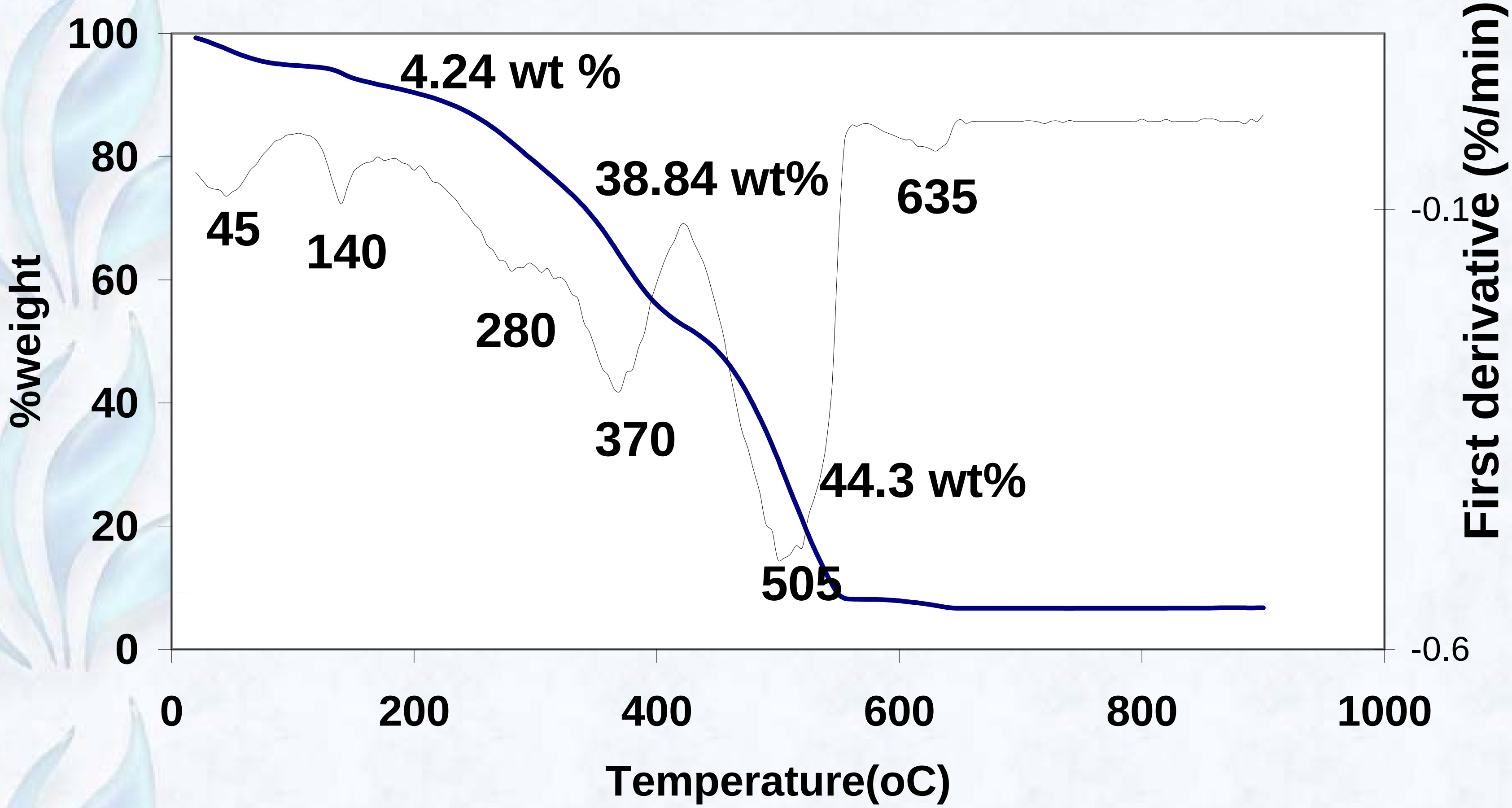
TG/DTG curves



Jute lignin decomposition occurs by two steps, the first one with peak temperature at 380 ^{o}C, the second is very large the maximum mass loss being found both at 510 and 545 ^{o}C.

The total mass loss is of 89.64 wt%.

TG/DTG curves



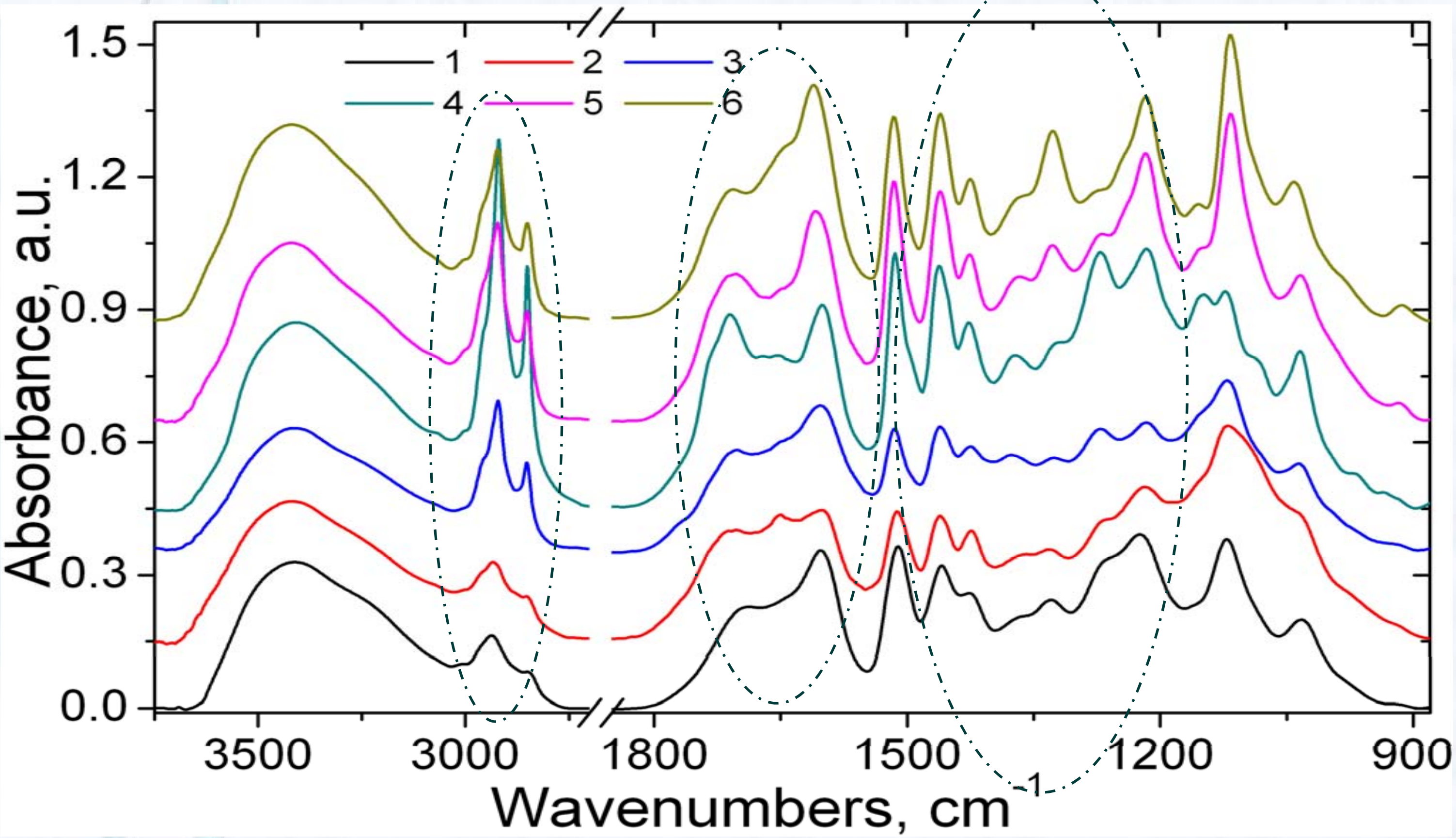
Sisal lignin decomposes in 5 peaks with the temperature corresponding to the maximum mass loss rate at 140, 280, 370, 505 and 635 ^{o}C. The total mass loss is 87.38 wt%.

TG/DTG curves

Sample	Total mass loss (wt%)
Bagasse	92.70
Straw	89.99
Hemp	86.91
Flax	90.82
Jute	89.64
Sisal	87.38

The TG/DTG curves are specific for each type of lignin could be considered as “thermal spectra” for lignin identification.

IR spectra



1 - Bagasse
2 - Straw
3 - Hemp
4 - Flax
5 - Jute
6 - Sisal

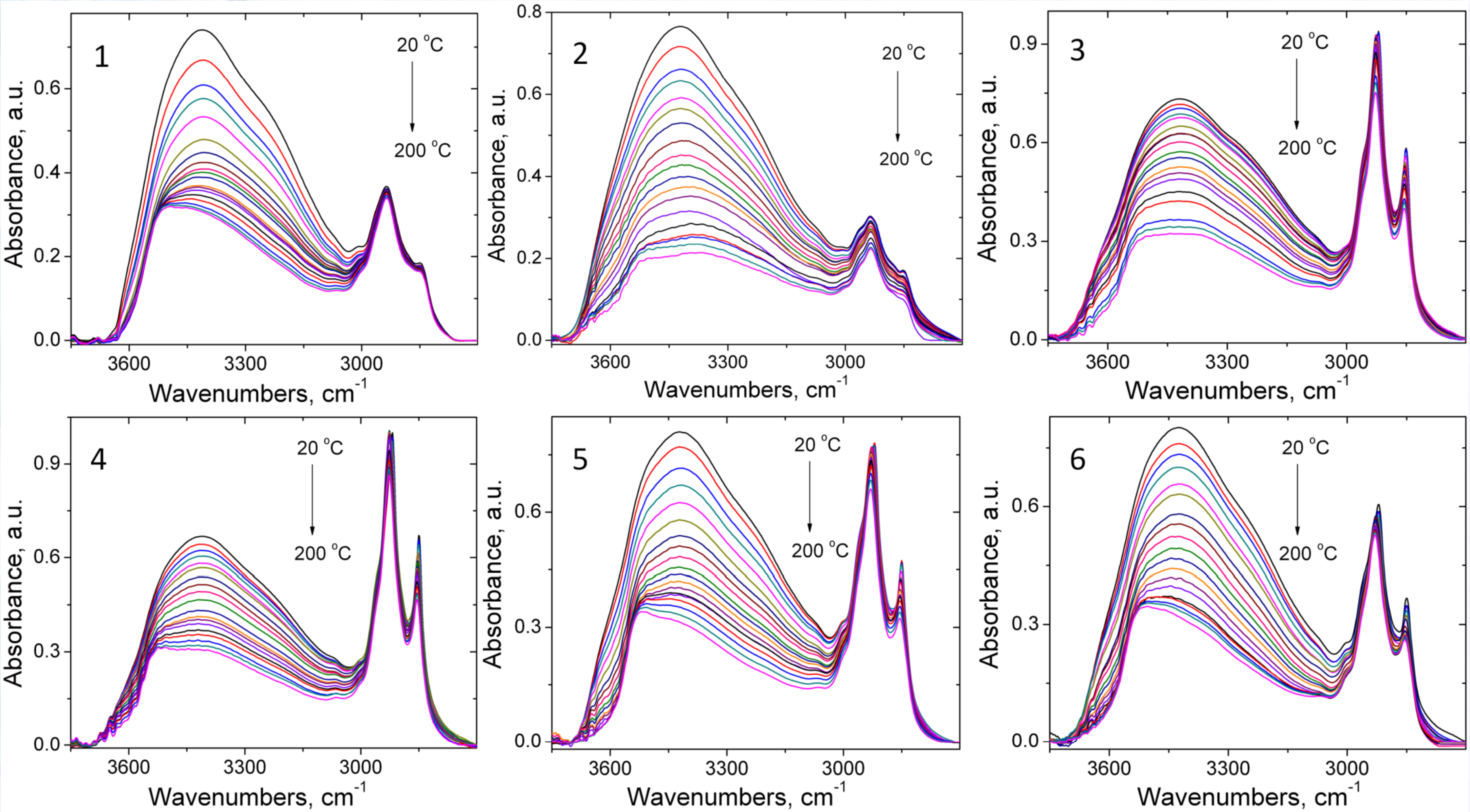
2930, 2850 cm^{-1} - CH symmetric and asymmetric stretching in aromatic methoxyl groups and in aliphatic methyl and methylene groups of side chains

1600, 1510 cm^{-1} – aromatic skeletal stretching vibration

1365, 1329 cm^{-1} - symmetric C-H bending from methoxyl group and C1-O vibrations in syringyl derivatives

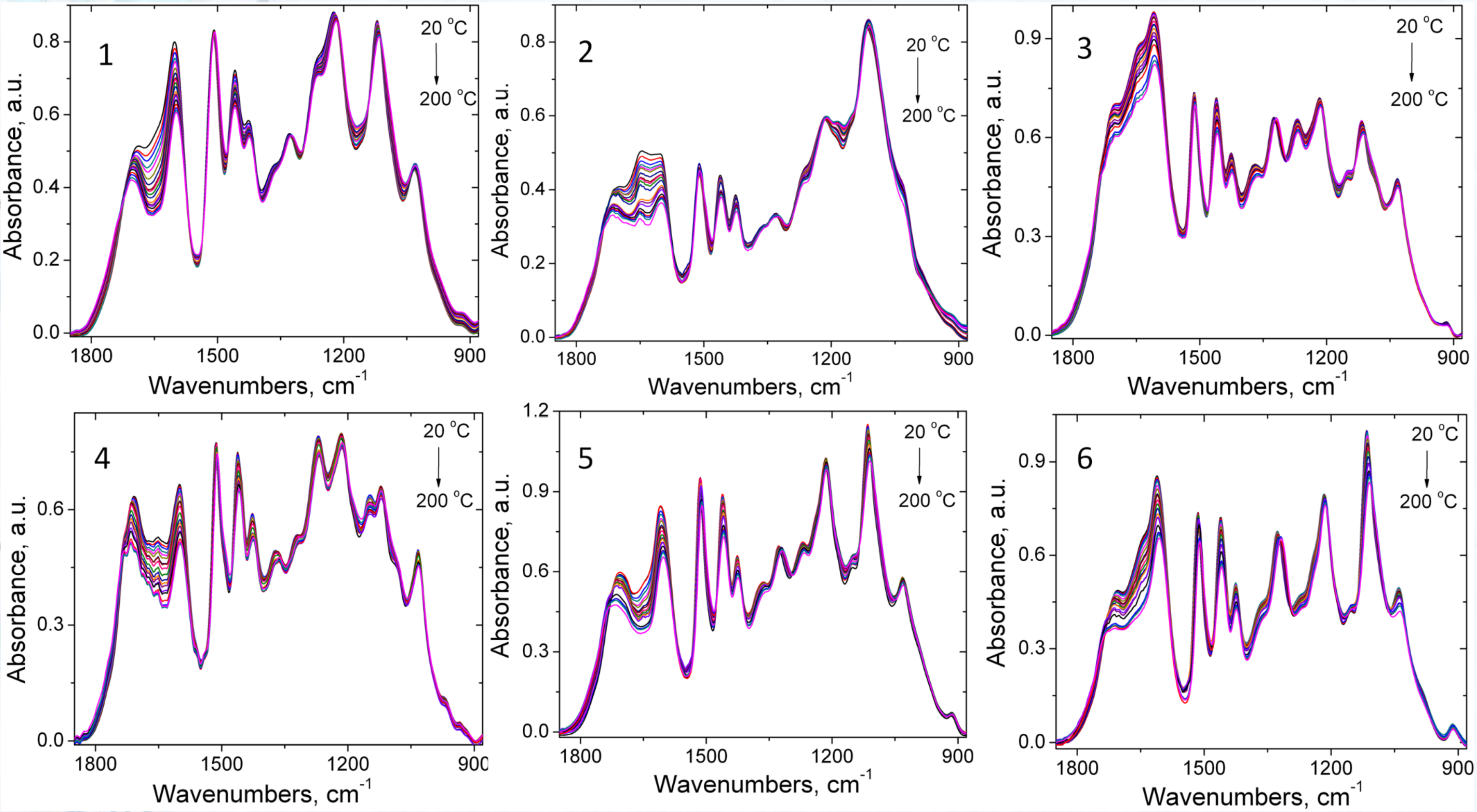
1030 cm^{-1} – C_{alkyl} – O ether vibrations methoxyl and β– O – 4 in guaiacol

Temperature induced structural changes in 3800-2700 cm^{-1} region



1 – Bagasse 2 – Straw 3 – Hemp 4 – Flax 5 – Jute 6 - Sisal

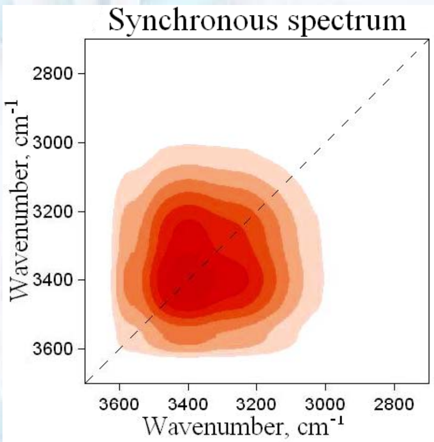
Temperature induced structural changes in 1900-900 cm^{-1} region



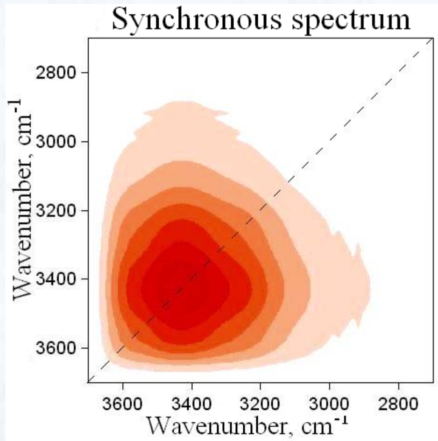
1 – Bagasse 2 – Straw 3 – Hemp 4 – Flax 5 – Jute 6 - Sisal

2D IR correlation spectra

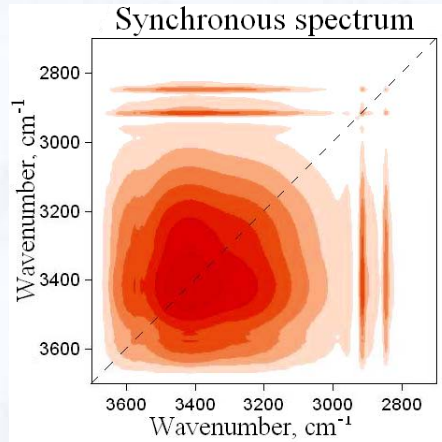
2D FTIR correlation intensities were calculated using the generalized 2D correlation method developed by Noda. For all calculations, the spectrum recorded at room temperature was used as reference spectrum.



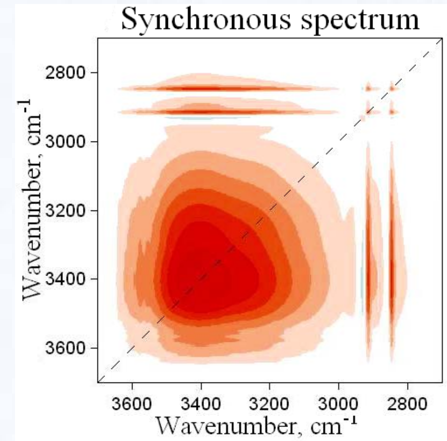
Bagasse



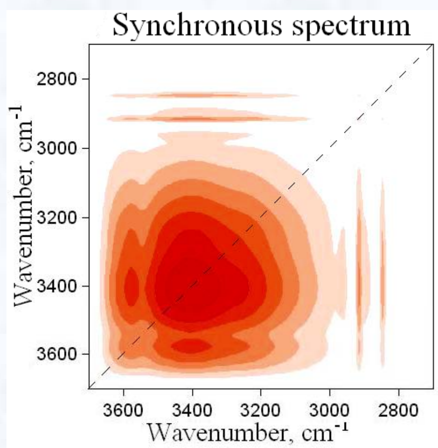
Straw



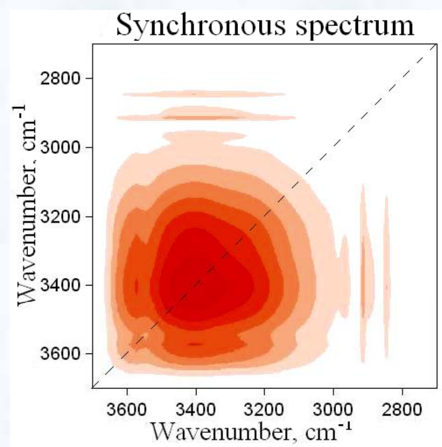
Hemp



Flax

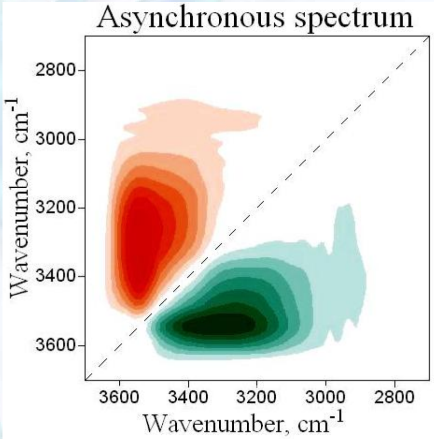


Jute

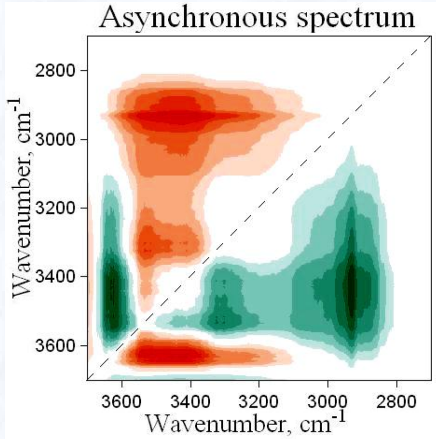


Sisal

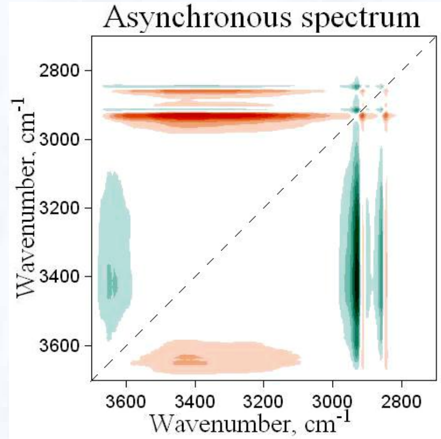
2D IR correlation spectra



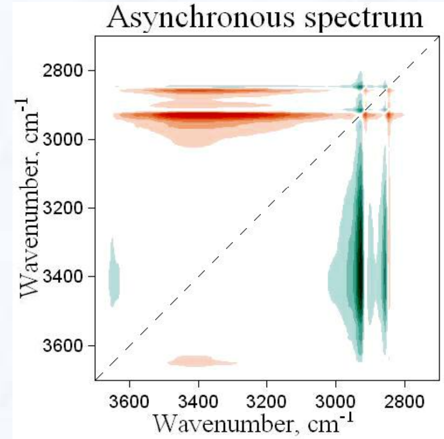
Bagasse



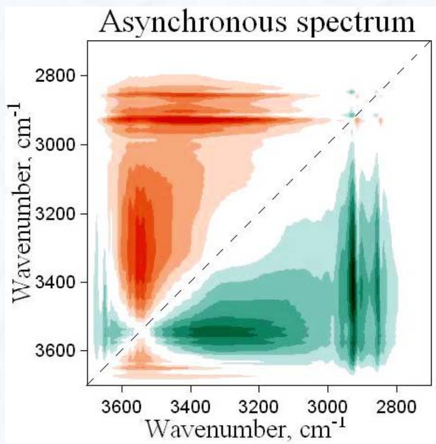
Straw



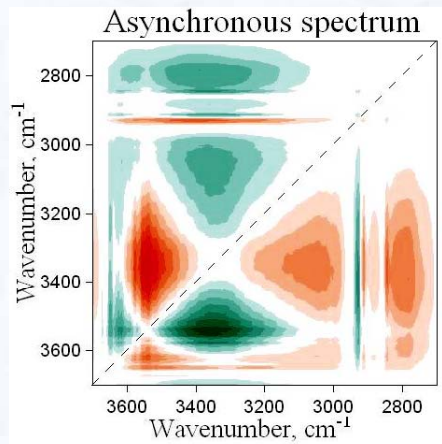
Hemp



Flax

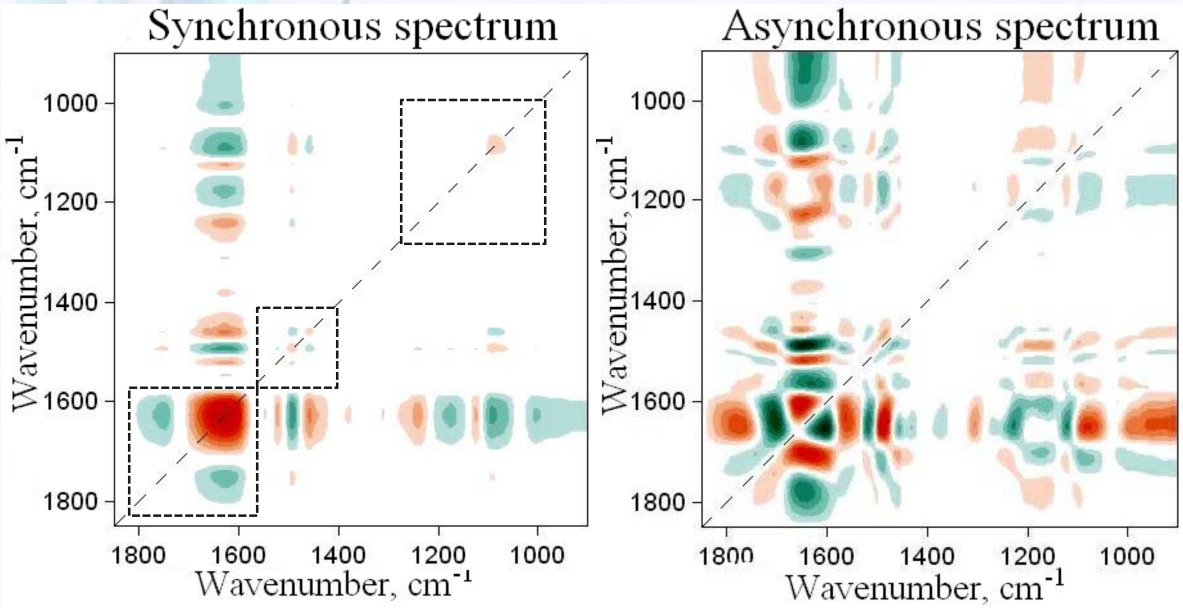


Jute



Sisal

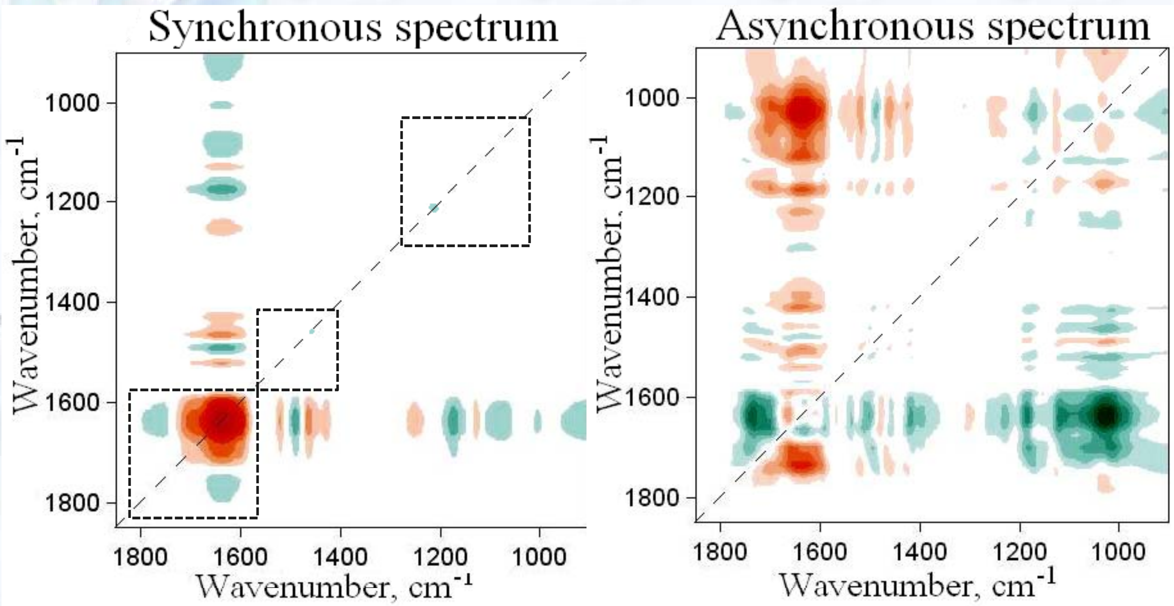
2D correlation spectra of bagasse lignin



New bands (cm⁻¹)	
Synchronous	Asynchronous
1752	1781
1491	1708
1177	1567
1005	1484
	1306
	1100

clusters	2x2 (1850 – 1550 cm^{-1})	3x3 (1550 – 1400 cm^{-1})	1x1 (1300 – 1000 cm^{-1})
auto-peaks	1628 cm^{-1}	1491, 1457 cm^{-1}	1090 cm^{-1}
cross-peaks	1752 vs. 1628 cm^{-1}	1491 vs. 1457 cm^{-1} 1522 vs. 1491 cm^{-1}	__

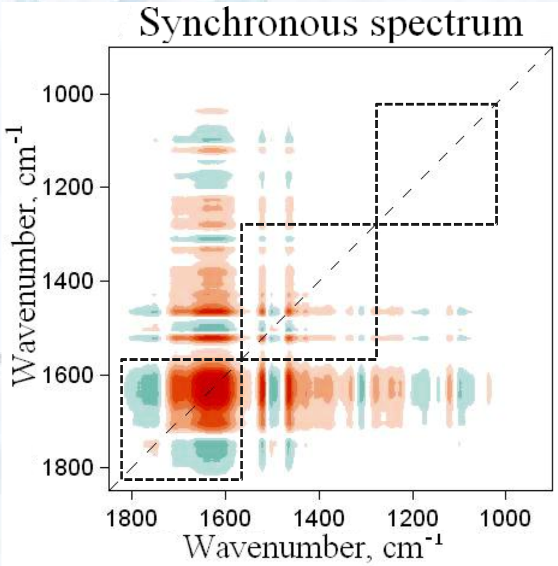
2D correlation spectra of straw lignin

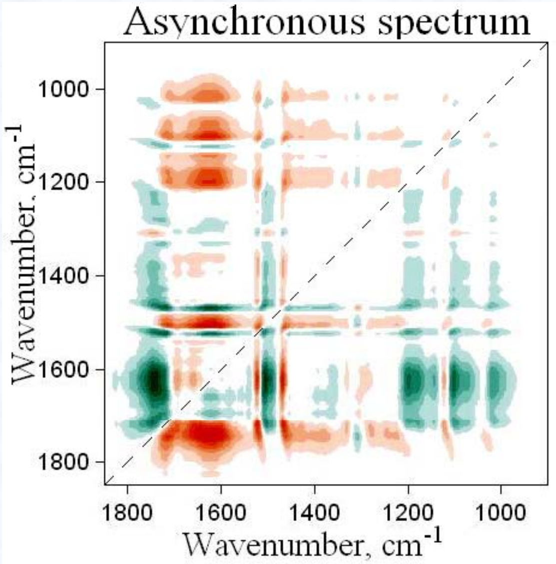


New bands (cm^{-1})	
Synchronous	Asynchronous
1765	1780
1527	1733
1497	1667
1175	1571
1078	1457
1010	1305
	1249
	1083

clusters	2x2 (1850 – 1550 cm^{-1})	1x1 (1550 – 1400 cm^{-1})	1x1 (1300 – 1000 cm^{-1})
auto-peaks	1639 cm^{-1}	1468 cm^{-1}	1175 cm^{-1}
cross-peaks	1765 vs. 1639 cm^{-1}	__	__

2D correlation spectra of hemp lignin

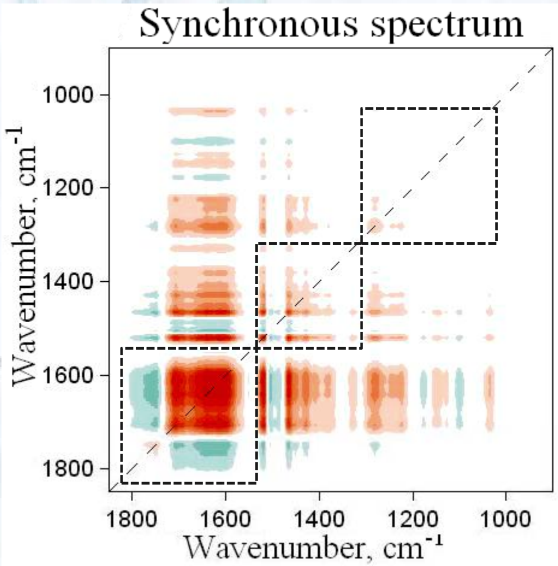


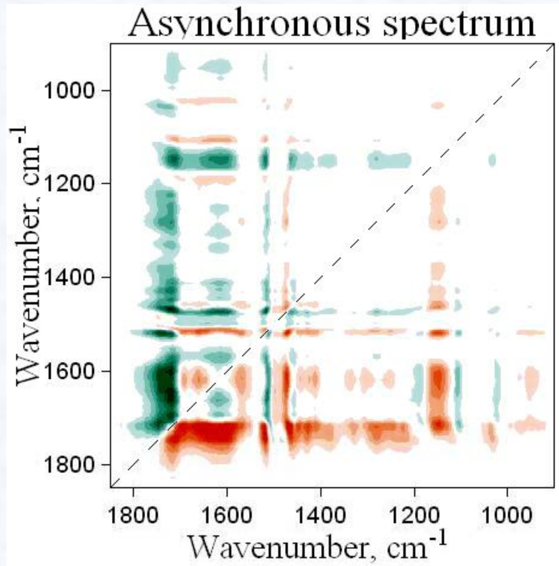


New bands (cm^{-1})	
Synchronous	Asynchronous
1751	1794
1405	1721
1307	1624
1244	1578
1176	1546
1144	1473
1077	1358
	1195
	1010

clusters	4x4 (1850 – 1550 cm^{-1})	6x6 (1550 – 1300 cm^{-1})	0x0 (1300 – 1000 cm^{-1})
auto-peaks	1751, 1707, 1639, 1615 cm^{-1}	1522, 1501, 1468, 1428 cm^{-1}	––
cross-peaks	1751 vs. 1615, 1639 cm^{-1} 1707 vs. 1615, 1639 cm^{-1} 1639 vs. 1615	1522 vs. 1501, 1468, 1428, 1405, 1385, 1336, 1307 cm^{-1} 1501 vs. 1468, 1428 cm^{-1} 1468 vs. 1428, 1405, 1385, 1336, 1307 cm^{-1}	––

2D correlation spectra of flax lignin

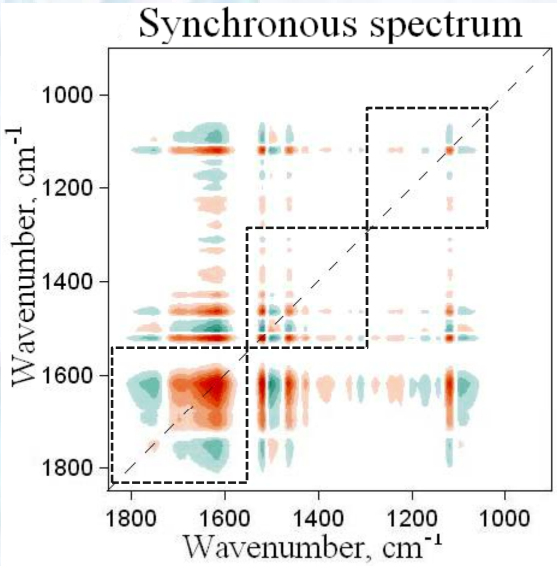


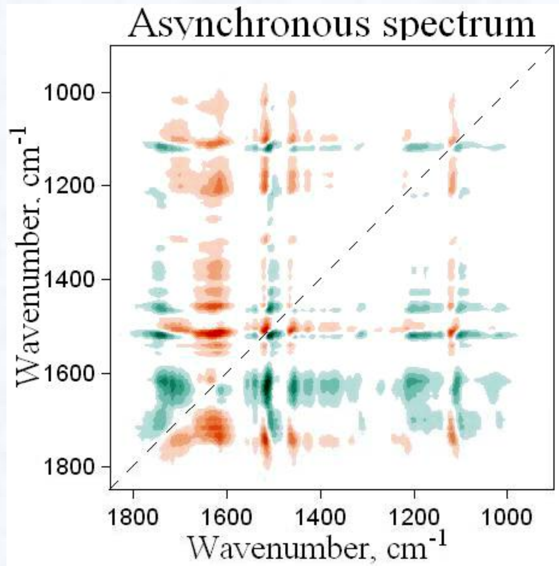


New bands (cm^{-1})	
Synchronous	Asynchronous
1751	1688
1639	1476
1561	1447
1249	1390
1105	1338
	1302
	1019

clusters	4x4 (1850 – 1550 cm^{-1})	6x6 (1550 – 1300 cm^{-1})	4x4 (1300 – 1000 cm^{-1})
auto-peaks	1751, 1702, 1639, 1613 cm^{-1}	1517, 1468, 1429 cm^{-1}	1283 cm^{-1}
cross-peaks	1751 vs. 1702,1639, 1613 cm^{-1} 1702 vs. 1639, 1613 cm^{-1} 1639 vs. 1613 cm^{-1}	1517 vs. 1500, 1468, 1429, 1380, 1329 cm^{-1} 1500 vs. 1468, 1429 cm^{-1} 1468 vs. 1429, 1380 cm^{-1} 1429 vs. 1380 cm^{-1}	1283 vs. 1249, 1224, 1034 cm^{-1}

2D correlation spectra of jute lignin

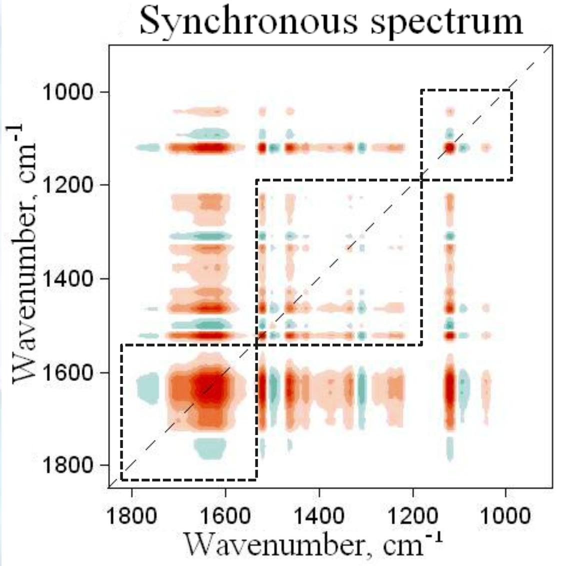


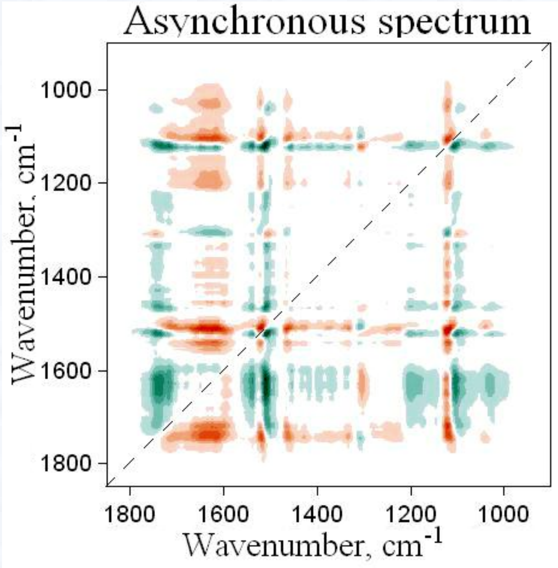


New bands (cm^{-1})	
Synchronous	Asynchronous
1762	1748
1497	1717
1308	1633
1247	1555
1176	1538
1093	1394

clusters	3x3 (1850 – 1550 cm^{-1})	9x9 (1550 – 1200 cm^{-1})	3x3 (1200 – 1000 cm^{-1})
auto-peaks	1695, 1617 cm^{-1}	1519, 1497, 1462 cm^{-1}	1122 cm^{-1}
cross-peaks	1762 vs. 1695, 1617 cm^{-1} 1695 vs. 1617 cm^{-1}	1519 vs. 1497, 1462, 1428, 1382, 1336, 1312, 1278, 1224 cm^{-1} 1497 vs. 1462, 1428 cm^{-1} 1462 vs. 1428, 1382, 1336, 1247, 1224 cm^{-1}	1176 vs. 1122 cm^{-1} 1122 vs. 1093 cm^{-1}

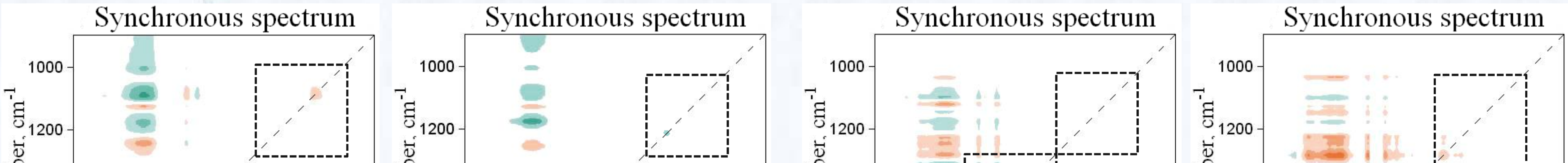
2D correlation spectra of sisal lignin





New bands (cm^{-1})	
Synchronous	Asynchronous
1761	1741
1499	1680
1305	1634
1249	1595
1092	1543
	1398
	1283
	1181

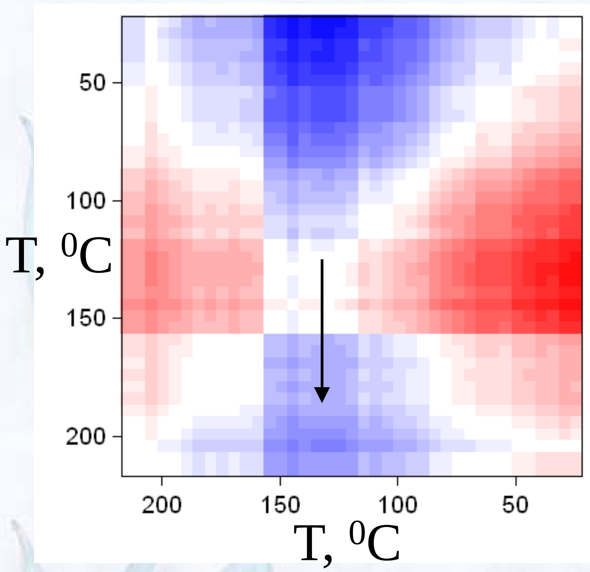
clusters	4x4 (1850 – 1550 cm^{-1})	9x9 (1550 – 1200 cm^{-1})	3x3 (1200 – 1000 cm^{-1})
auto-peaks	1707, 1642, 1615 cm^{-1}	1525, 1499, 1462, 1427, 1336, 1278 cm^{-1}	1119 cm^{-1}
cross-peaks	1761 vs. 1615, 1642 cm^{-1} 1707 vs. 1615, 1642 cm^{-1} 1642 vs. 1615 cm^{-1}	1525 vs. 1499, 1462, 1427, 1375, 1336, 1305, 1278, 1249, 1227 cm^{-1} 149 vs. 1462, 1427, 1336, 1305, 1227 cm^{-1} 1462 vs. 1427, 1375, 1336, 1305, 1278, 1249 cm^{-1} 1427 vs. 1336, 1305, 1227 cm^{-1} 1336 vs. 1305, 1249, 1227 cm^{-1} 1305 vs. 1227 cm^{-1}	1119 vs. 1092, 1042 cm^{-1}



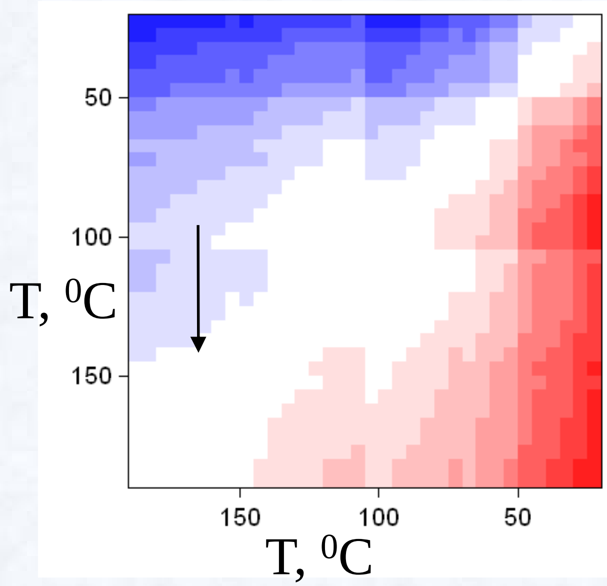
Sample	1850 – 1550 cm^{-1}	1550 – 1300 cm^{-1}	1300 – 1000 cm^{-1}
Bagasse	2x2	3x3	1x1
Straw	2x2	1x1	1x1
Hemp	4x4	6x6	0x0
Flax	4x4	6x6	4x4
Jute	3x3	9x9	3x3
Sisal	4x4	9x9	3x3

Jute *Sisal*

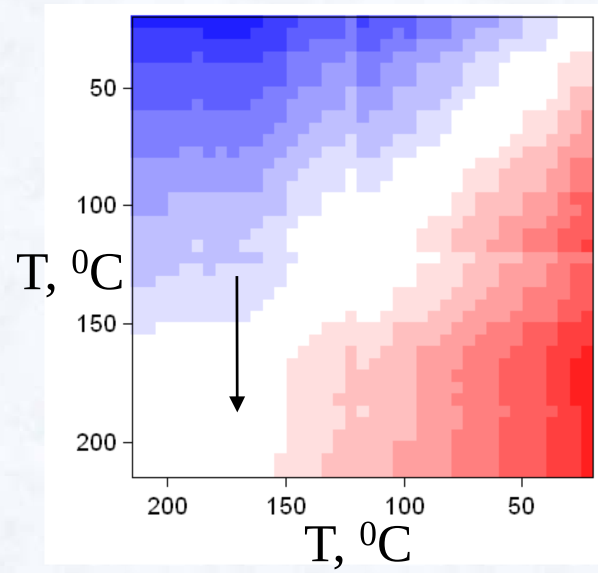
The different lignins have particular auto-peak clusters



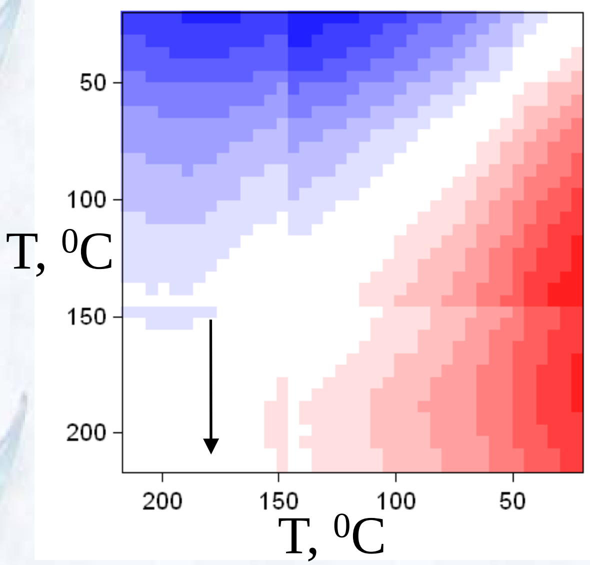
Bagasse



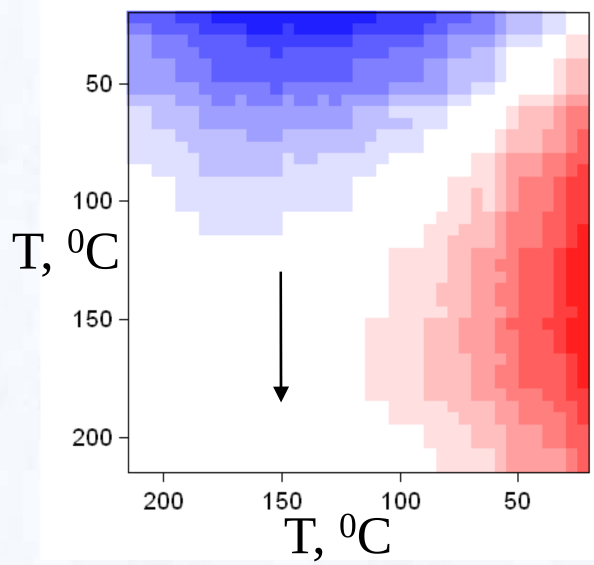
Hemp



Straw



Jute



Sisal

Glass transition temperatures evaluated from 2D IR correlation spectroscopy and DSC

Sample	Tg , ^{o}C (FT-IR)	Tg , ^{o}C (DSC)
Bagasse	138	142
Straw	180	175
Hemp	143	140
Flax	134	136
Jute	133	131
Sisal	125	121

Conclusions

- Thermal analysis can be used to measure the softening temperature, temperature corresponding to the glass transition, degradation temperature, and the durability of lignin
- The DSC study has shown that, as long as careful experimental procedures are followed, interesting differences of thermal behavior can be found which are characteristic of lignin origin and extraction method. However the structural differences play the most important role
- Different lignins can be primarily discriminated according to the position and intensities of the characteristic peaks in their IR spectra, so IR spectra can be regarded as the first step of their identification
- The 2D IR correlation spectra are another step and the most sensitive one of studied samples identification