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# Understanding the Variables that Define Tg for Kraft Lignin

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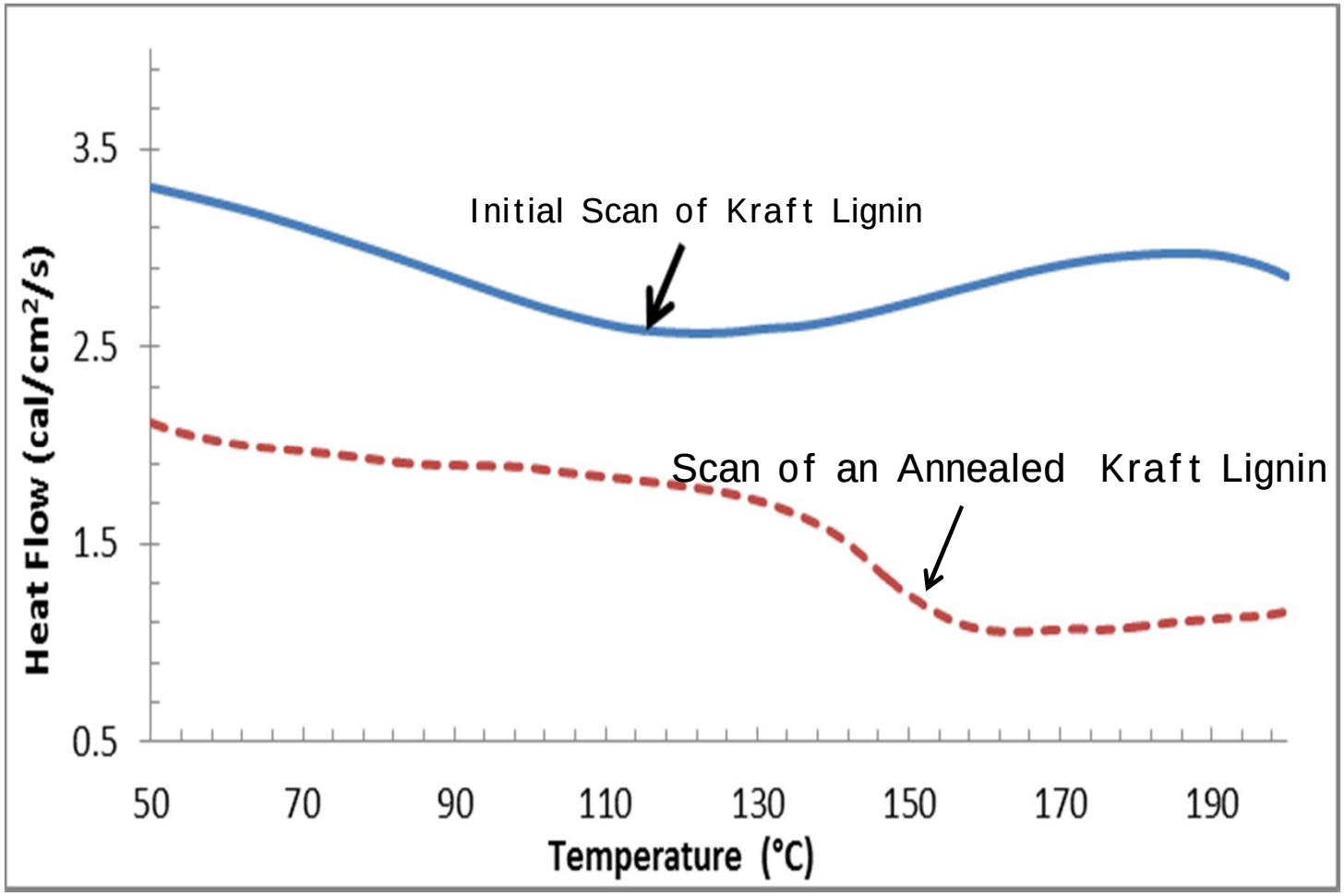
# Objective

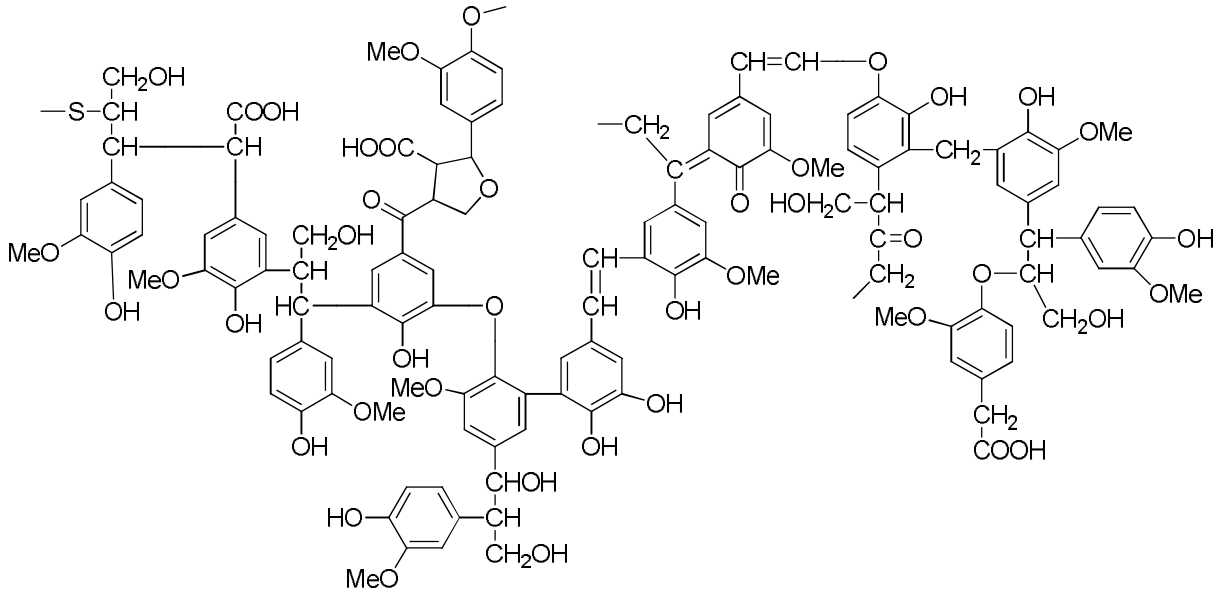
To determine the optimum temperature for annealing Technical Lignins based on the underlying chemical & polymeric factors that determine the value of Tg

# Why Do we Need to Anneal prior to Tg Determination?

- During its manufacturing history when a polymer is cooled to a temperature below its Tg, the polymer chains are likely to be frozen into a non-equilibrium glassy state.
- Once such a sample is subjected to a DSC scan, an endothermic enthalpy relaxation process usually occurs and this may affect the actual Tg determination measurement.
- For this reason it is often recommended to subject the sample to an initial scan (beyond its Tg) so as to eliminate the thermal history stored within the polymer's amorphous non-equilibrium configuration


Initial Scan of Kraft Lignin
Scan of an Annealed Kraft Lignin
Heat Flow (cal/cm²/s)
3.5
2.5
1.5
0.5
50
70
90
110
130
150
170
190
Temperature (°C)

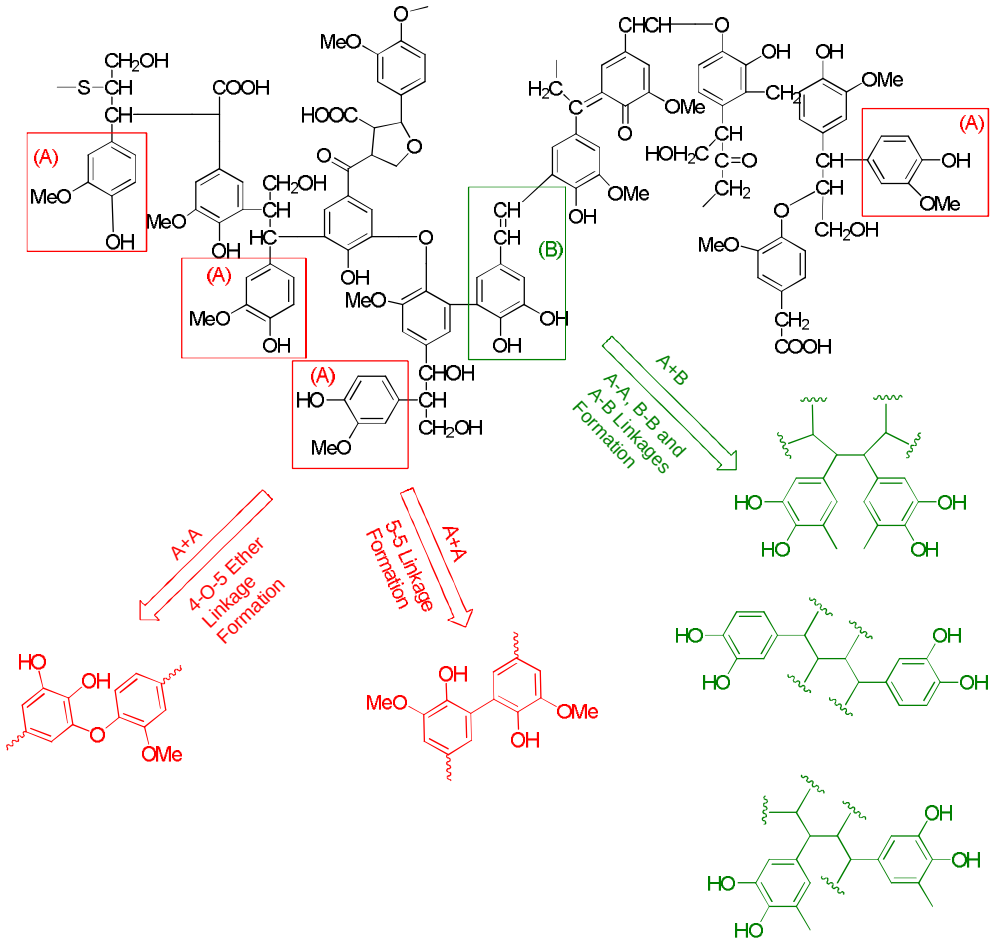
# Kraft Lignin Structure




Softwood kraft lignin is highly susceptible to thermally induced reactions that cause its molecular characteristics to be severely altered. These events seriously interfere and prevent such materials from being considered as candidates for thermoplastic applications.

*Marton, J. 1971.*

# A multitude of inter & intra molecular thermal events in Kraft lignin may operate via its phenolic OH groups.



# Starting Softwood Kraft Lignin "Indulin"

Molecular Weight :

Mw = 8000 (g/mol)

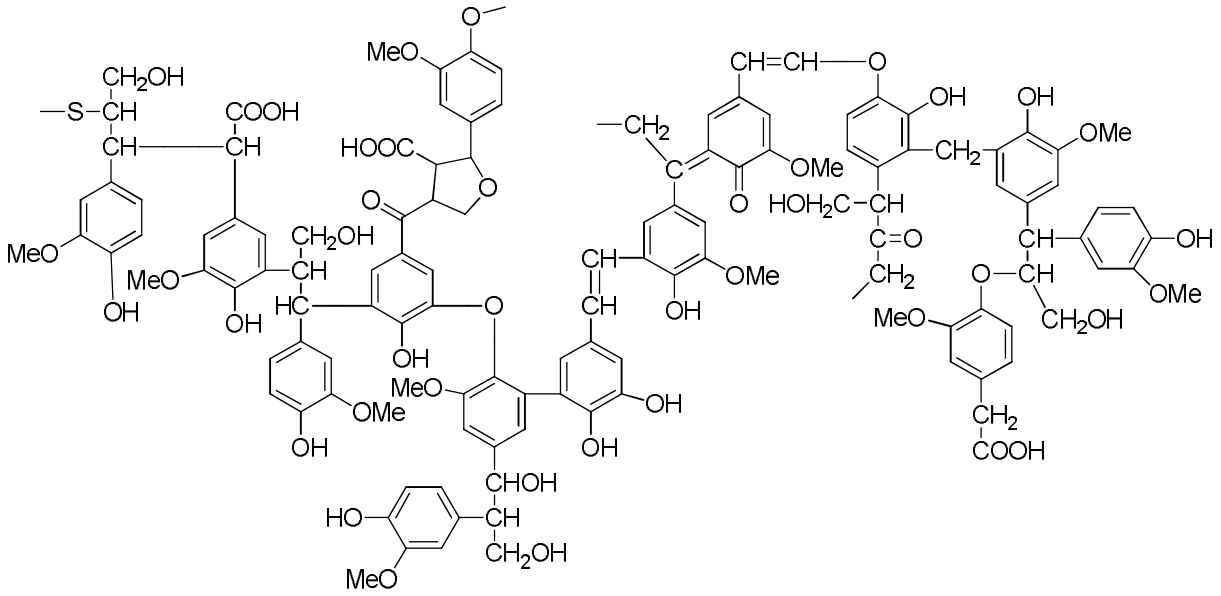
Mn = 2000 ( g/mol)

( Mw/Mn = 4 )

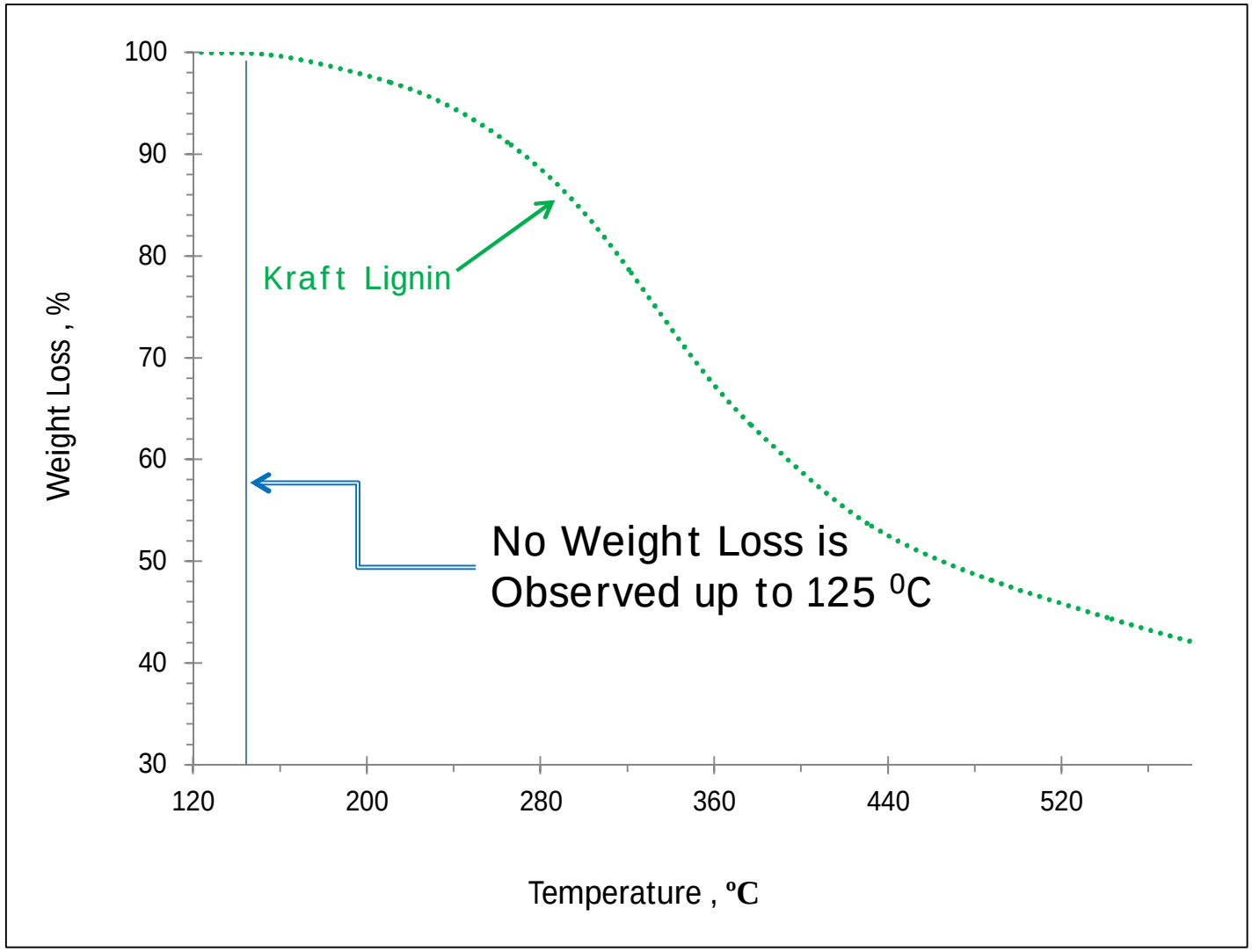
Total phenolic-OH = 3.85 mmol/ g

Total Aliphatic-OH = 2.4 mmol/g

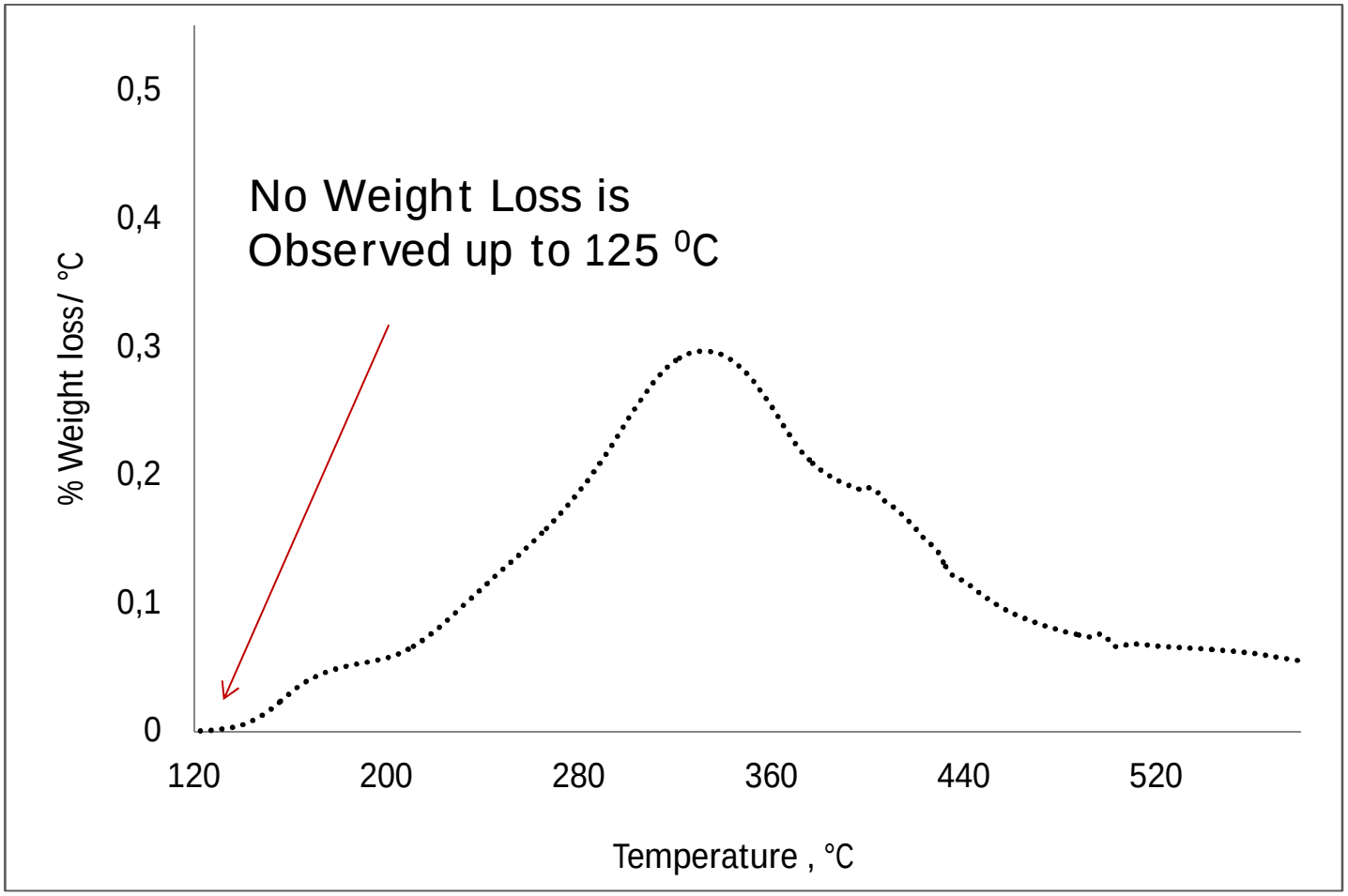
Tg : 150-160°C .



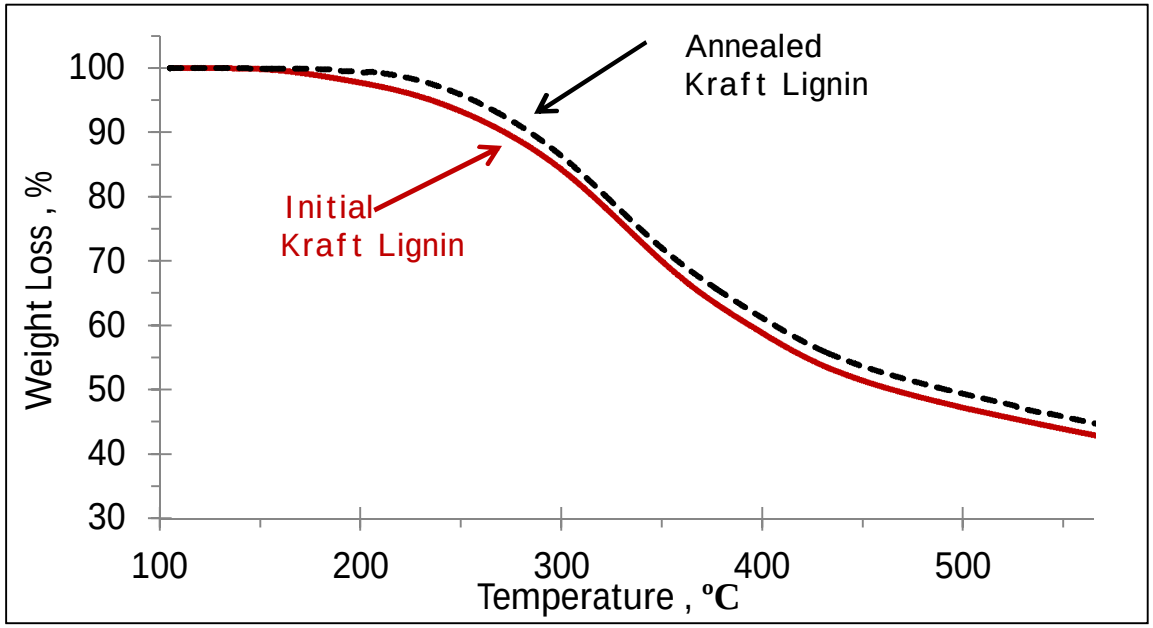
# TGA Thermograph of Kraft Lignin



# Derivative Thermogram for Kraft Lignin



# TGA Thermograms for Kraft Lignin Before & After Annealing Above its Tg for 20 mins



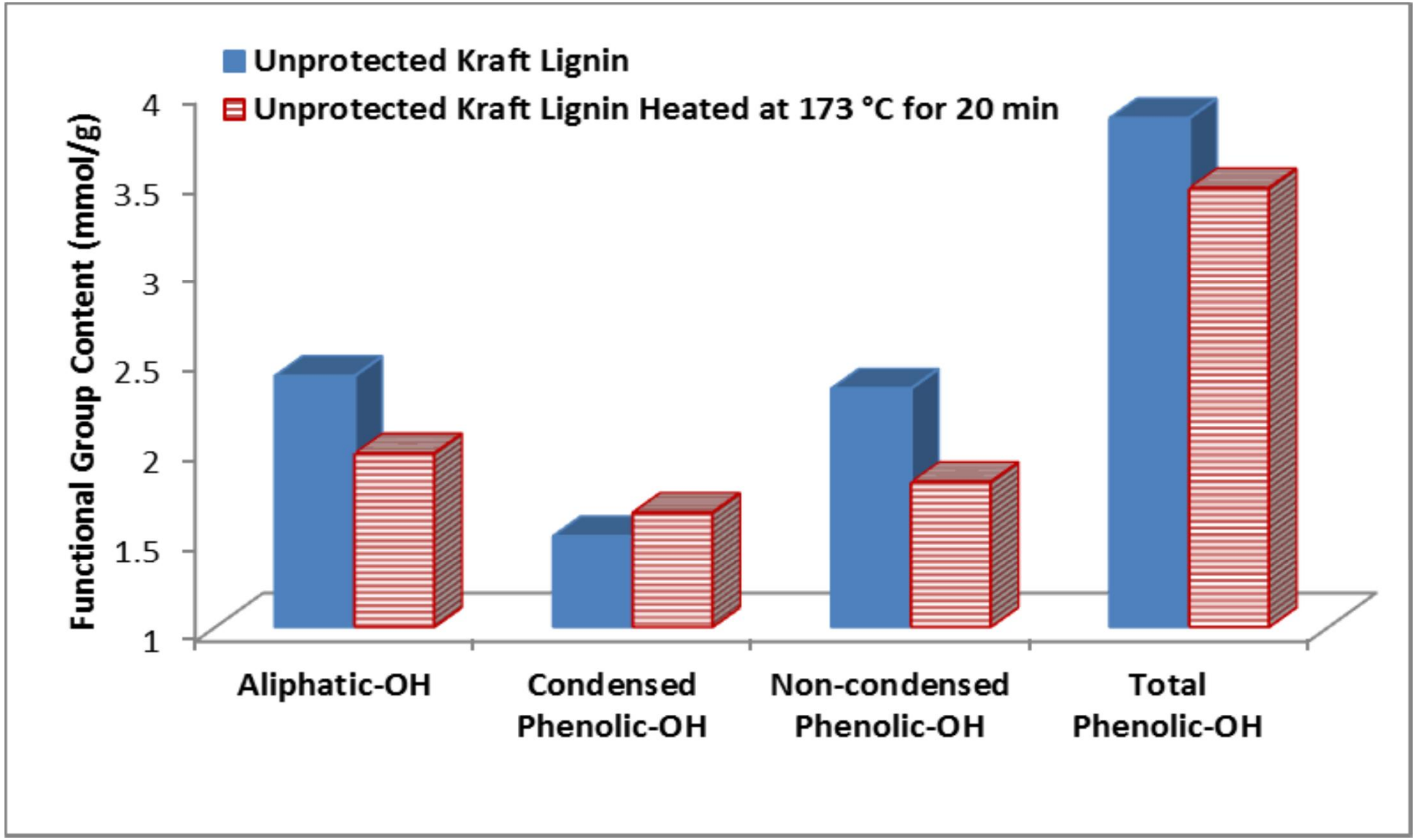

| Sample Weight Loss | | Td , Temperature , °C | | |
|---|---|---|---|---|
| | | **1%** | **2%** | **5%** |
| Kraft Lignin | Before | **176** | 195 | 235 |
| | After Annealing | 215 | 230 | 256 |
| | ΔT , ºC | +29 | +35 | +19 |

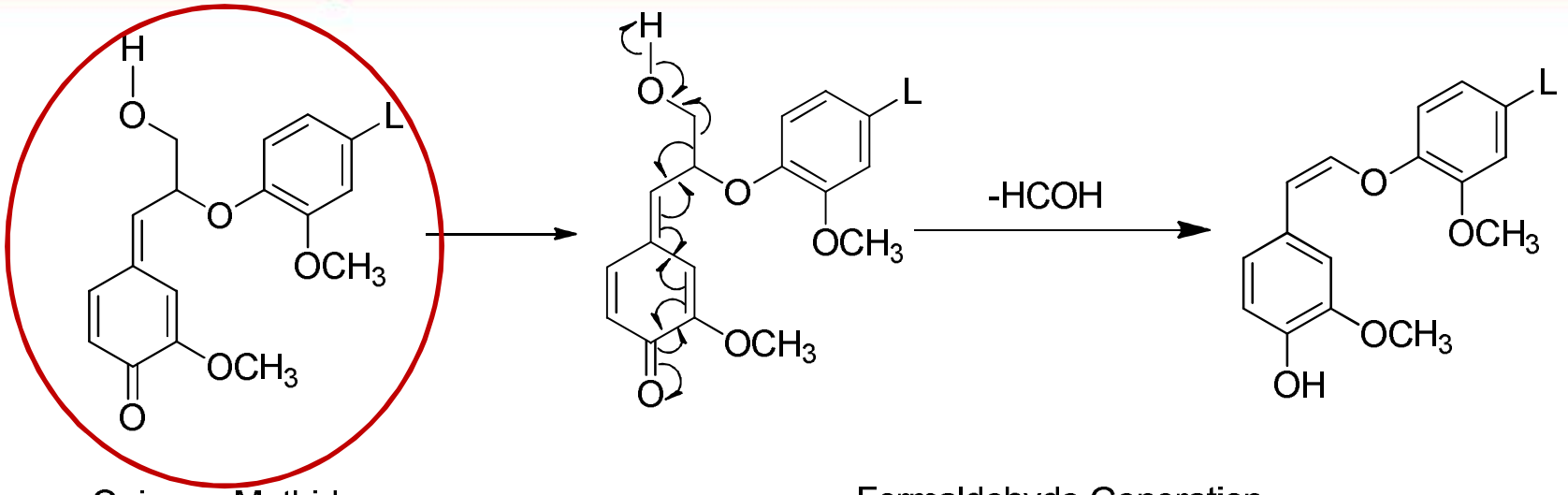
The Thermal Decomposition behavior of Kraft Lignin was changed after Annealing above its Tg

It seems that annealing induces changes within the lignin structure

leading to greater thermal stability .

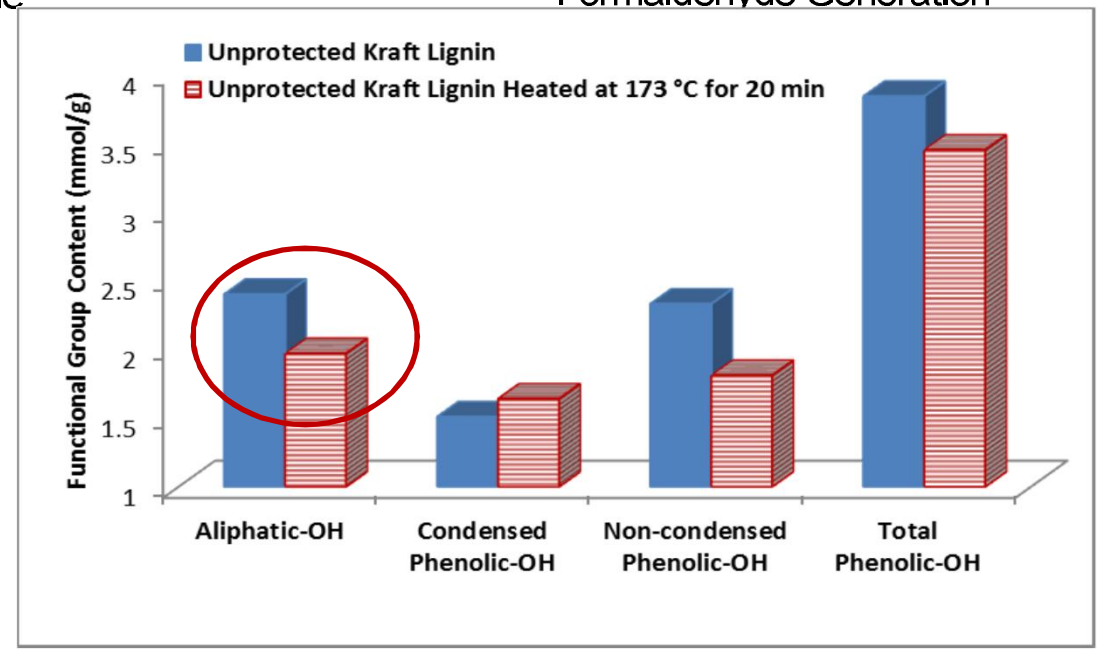
# Functional Group Distributions of Heated Kraft Lignin ($^{31}$P NMR)


Unprotected Kraft Lignin
Unprotected Kraft Lignin Heated at 173 °C for 20 min
Functional Group Content (mmol/g)
4
3.5
3
2.5
2
1.5
1
Aliphatic-OH
Condensed Phenolic-OH
Non-condensed Phenolic-OH
Total Phenolic-OH

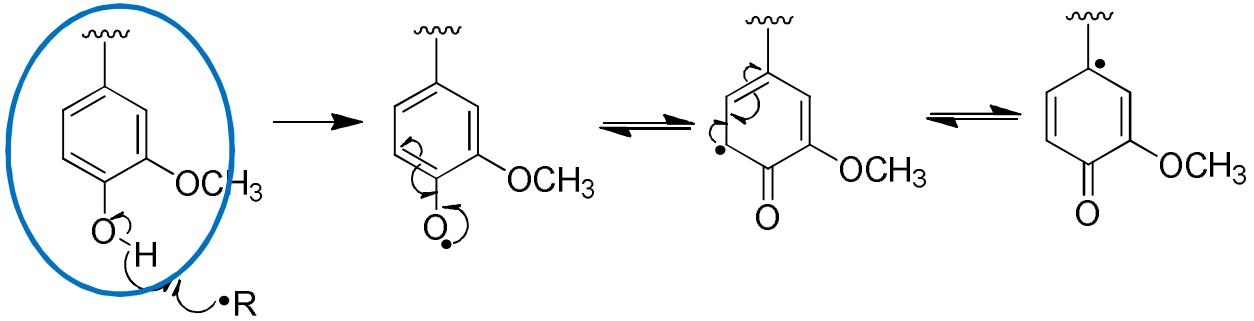


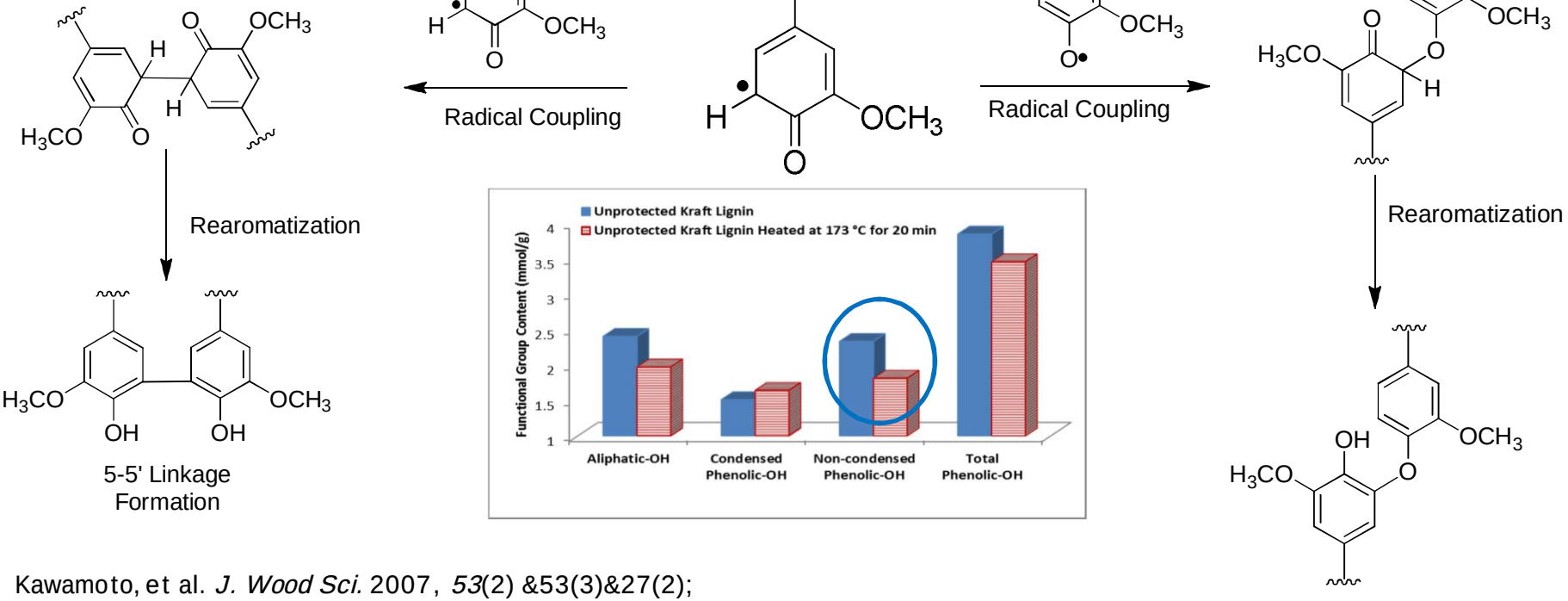

Quinone Methide

Formaldehyde Generation

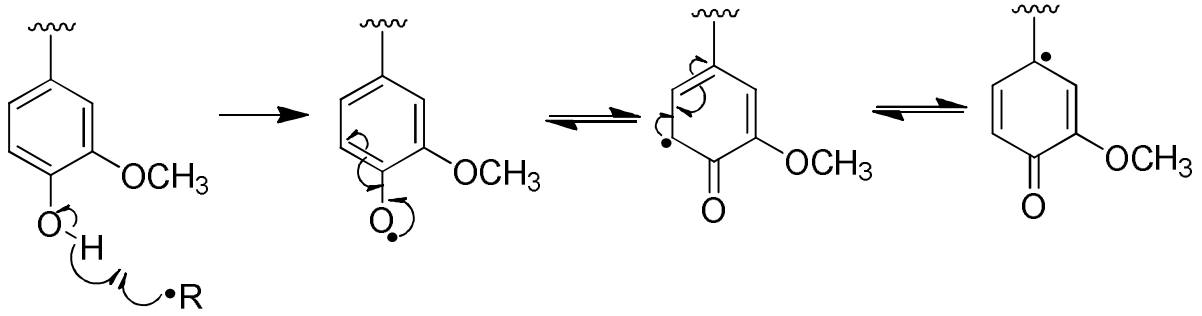


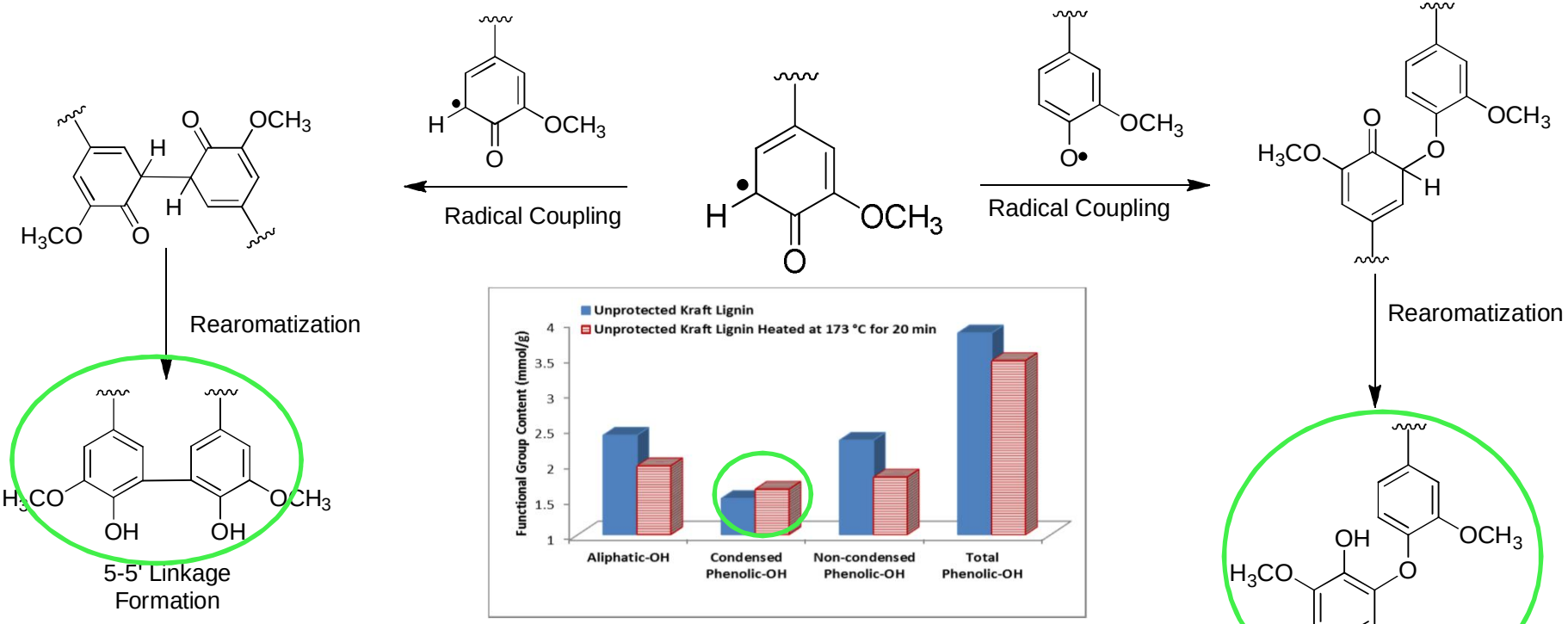

Kawamoto,et al, *J. Wood Chem. Technol.* 2007, *27* (2), 113-120.; *Holzforschung* 2008, *62* (1), 50



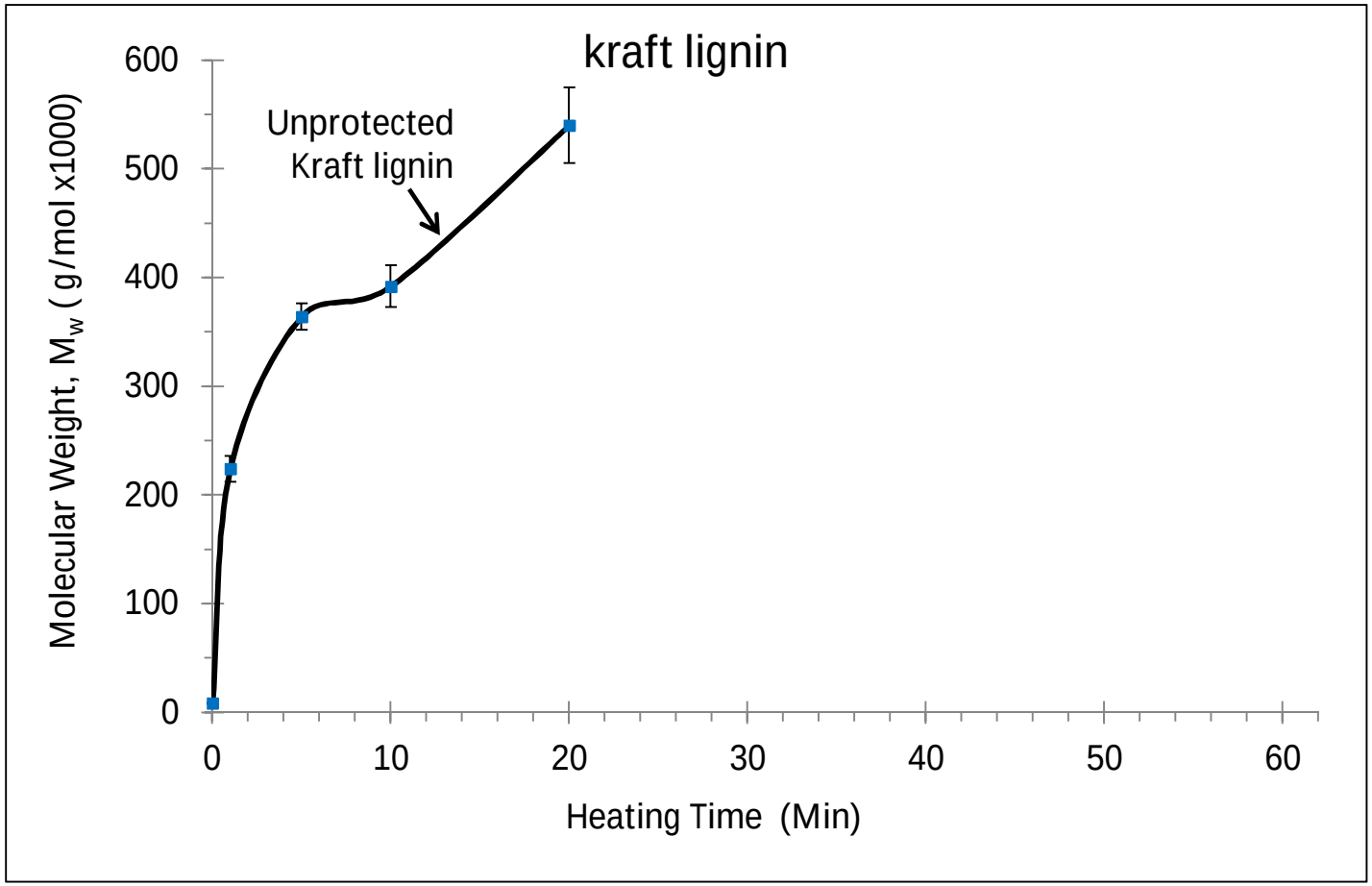

Kawamoto, et al. *J. Wood Sci.* 2007, *53*(2) &53(3)&27(2);
*J. Anal. Appl. Pyrolysis* 2008, *81* (1), 88-94.
*Holzforschung* 2008, *62* (1), 50.
Ohashi, et al.. *Org. Biomol.. Chem.* 2011, *9* (7), 2481-2491



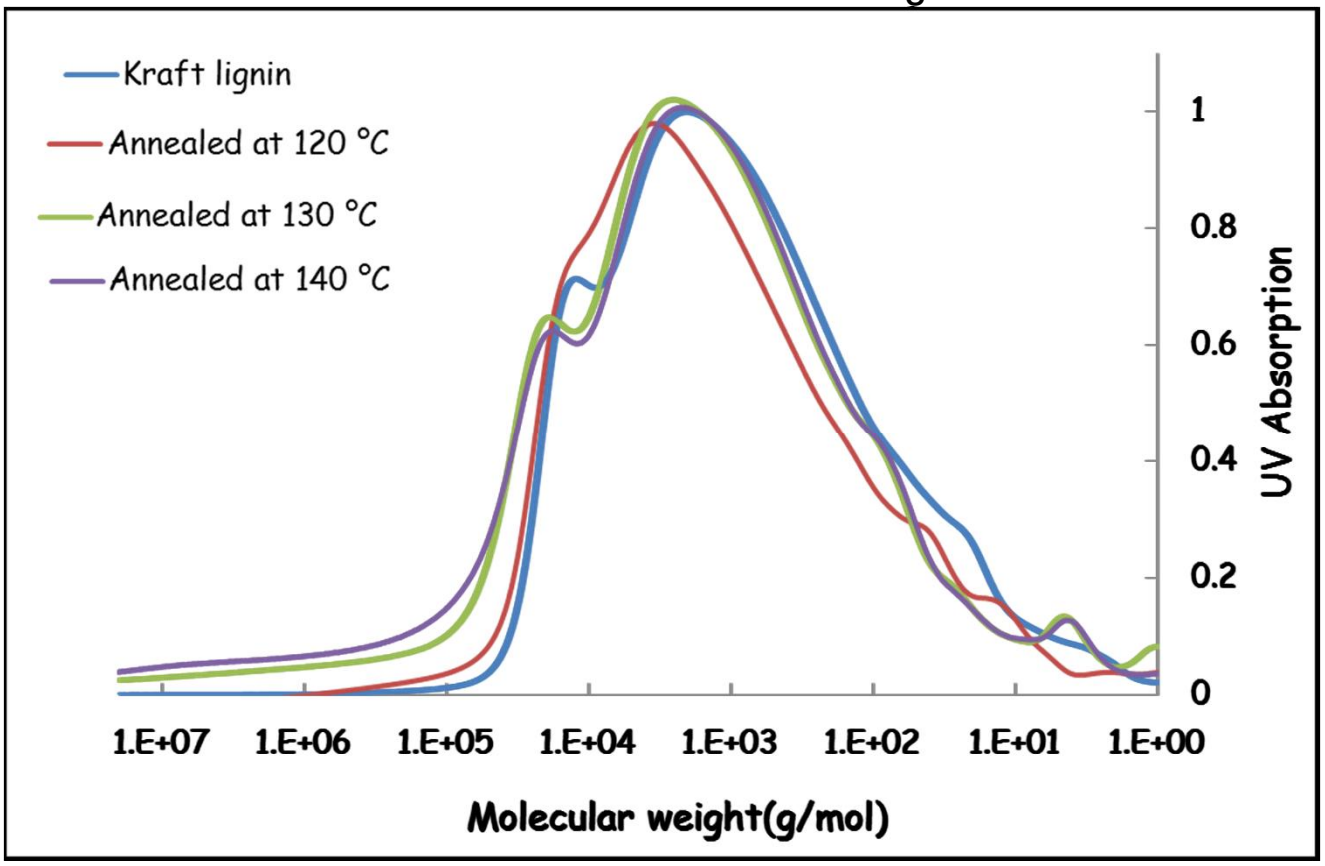




Kawamoto, et al. *J. Wood Sci.* 2007, *53*(2) &53(3)&27(2);
*J. Anal. Appl. Pyrolysis* 2008, *81* (1), 88-94.
*Holzforschung* 2008, *62* (1), 50.
Ohashi, et al.. *Org. Biomol.. Chem.* 2011, *9* (7), 2481-2491

# Effect of Heating Kraft Lignin 20 $^0$C above Tg on Molecular Weight



# Effect of Heating Between 120-140 °C on the Mol. Wt. Distribution of Kraft Lignin

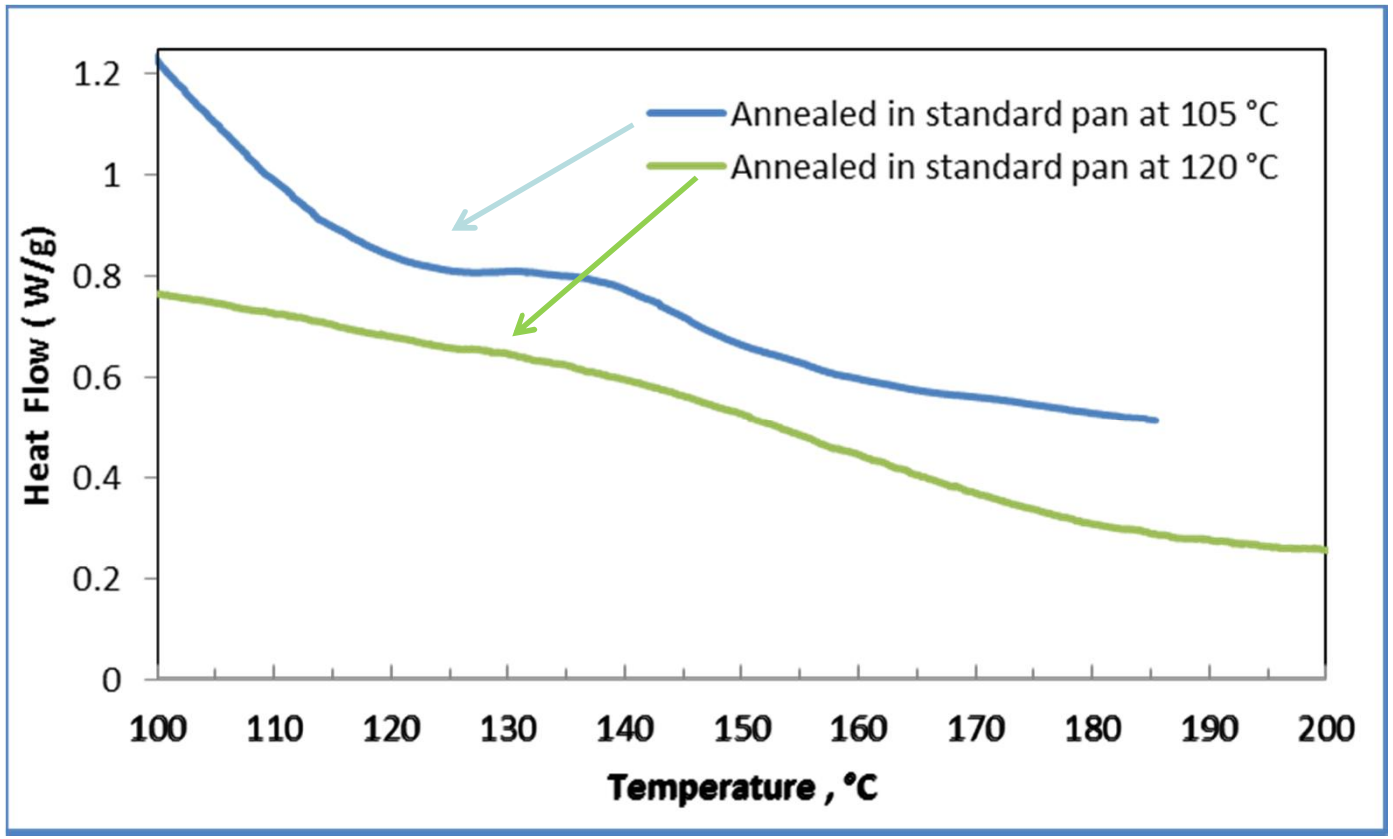



| Annealing Temperature, ℃ | --- | 120 | 130 | 140 |
|---|---|---|---|---|
| Mw (g/mol) | 8000 | 13000 | 128000 | 340000 |
| Mn ( g/mol) | 2000 | 2030 | 2200 | 2100 |
| Mw/Mn | 4 | 6.4 | 58.2 | 162 |

# Effect of DSC Pan Type

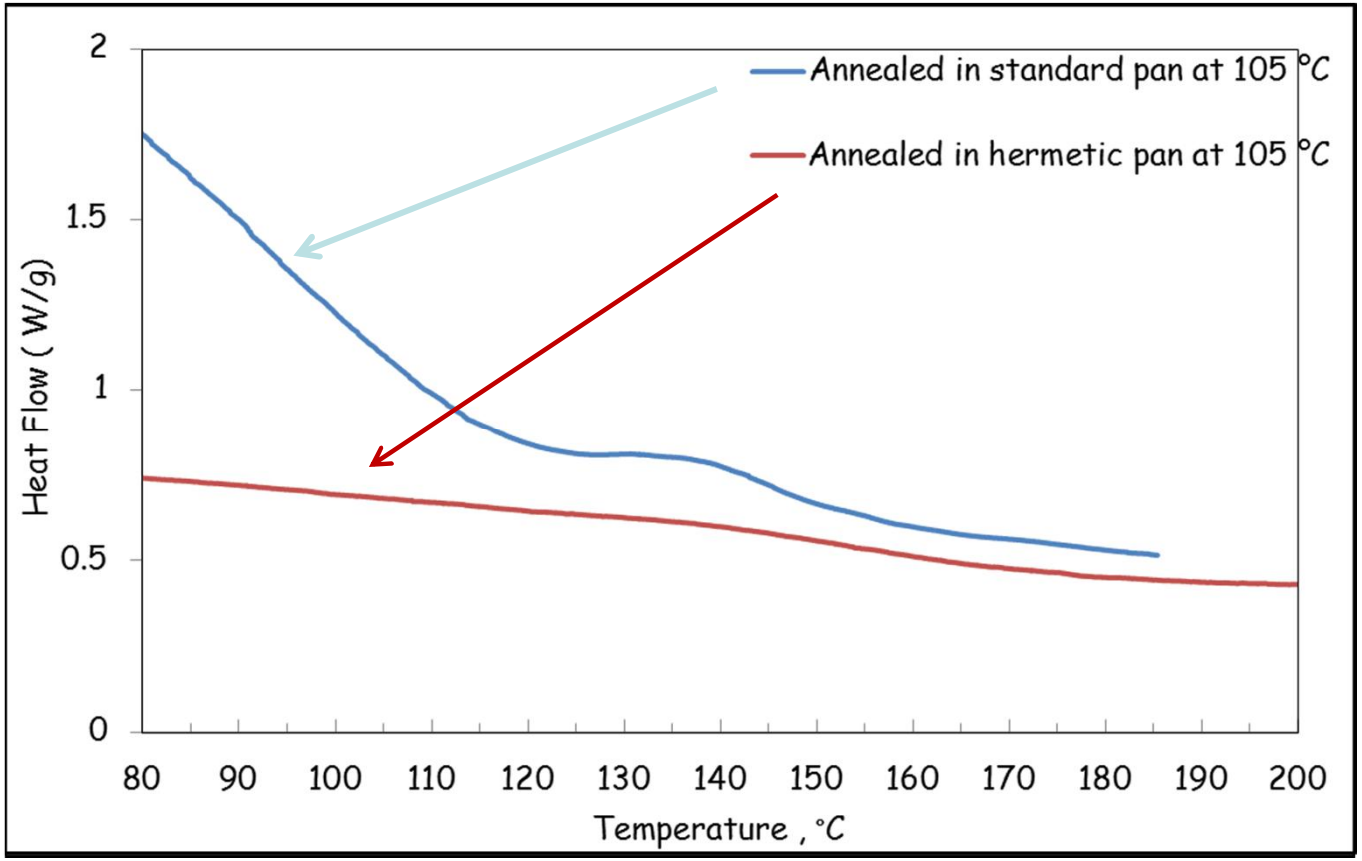
- Conventional Pan
- Hermetically Sealed Vented Pan

Effect of annealing at 105 °C and 120 °C for 30 min on Tg determination of kraft lignin using standard DSC pan



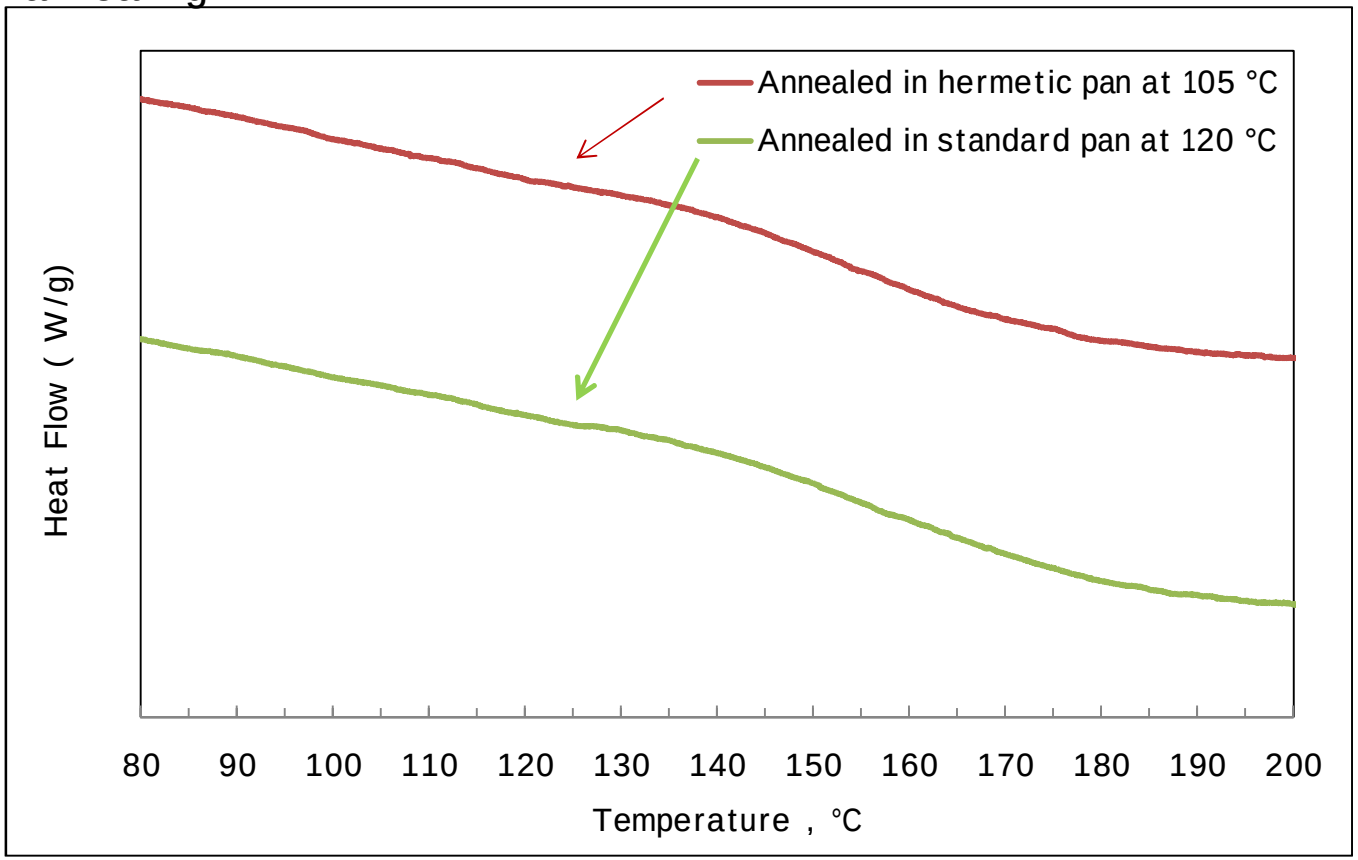

Using a standard pan shows that annealing at 120 °C is an acceptable temperature

Effect of annealing at 105 °C for 30 min on Tg determination of kraft lignin using standard and hermetic ( with hole on the lid ) DSC pan




With same procedure, vented hermetic DSC pan, shows smoother data than the standard pan.

Effect of standard and hermetic DSC pan on Tg determination of lignin after annealing.




Annealing of kraft lignin at 120 °C in standard pan showed a Tg of 155°C
Annealing of kraft lignin at 105 °C in a vented hermetic pan showed a Tg of 152°C

# Conclusions

Annealing Kraft Lignin at 105$^0$C with a vented hermetically sealed pan seems to be an acceptable set of conditions

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# Round Robin Tg Determination Study Conducted by Inventia

## Our Contribution

# Tg Determination Procedure Applied

Applied in Triplicate:

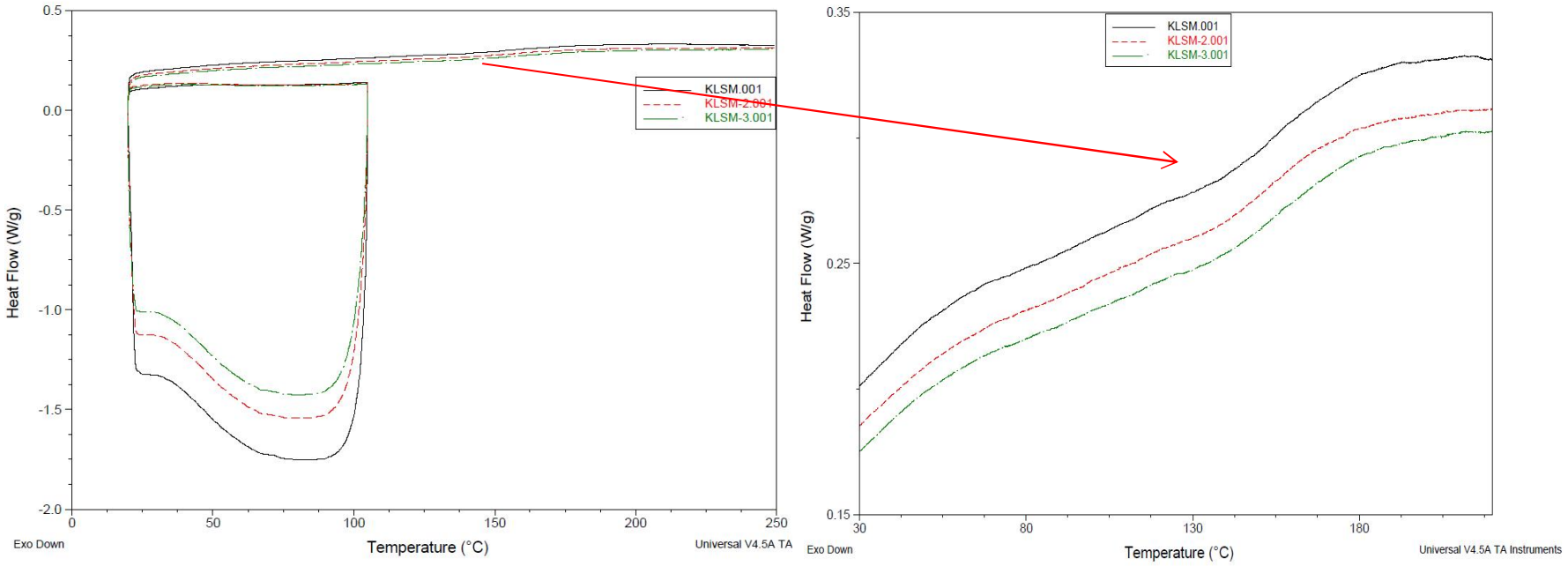
Drying/Annealing Cycle

1. Ramp 1 $^0$C/min up to 105 $^0$C
2. Isothermal Treatment at 105 C for 20min
3. Quench to 20 $^0$C
4. Isothermal Scan at 20 $^0$C for 10 minutes.

Test cycle

1. Ramp 3 $^0$C/min up to 250 $^0$C
2. End of test

# DSC Thermograms for KLSM Lignin, Kraft Softwood Lignin

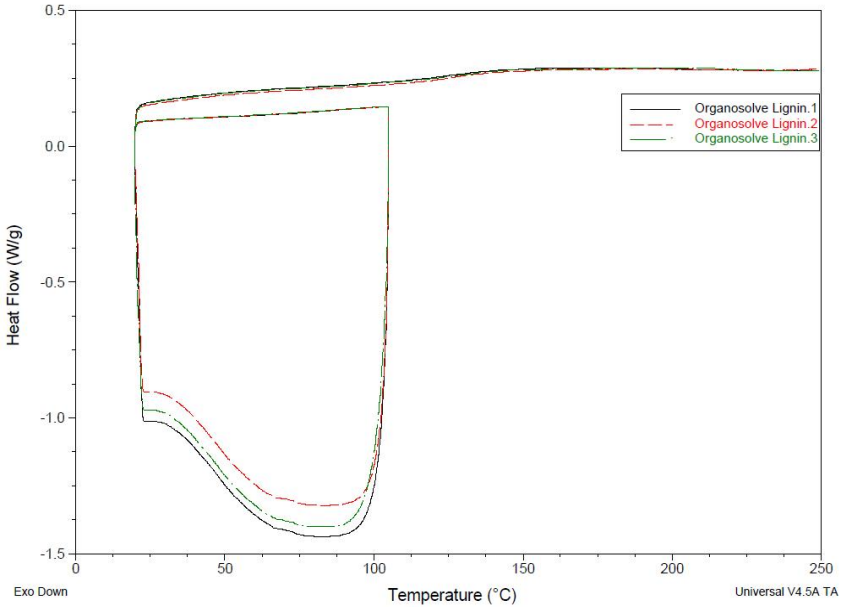


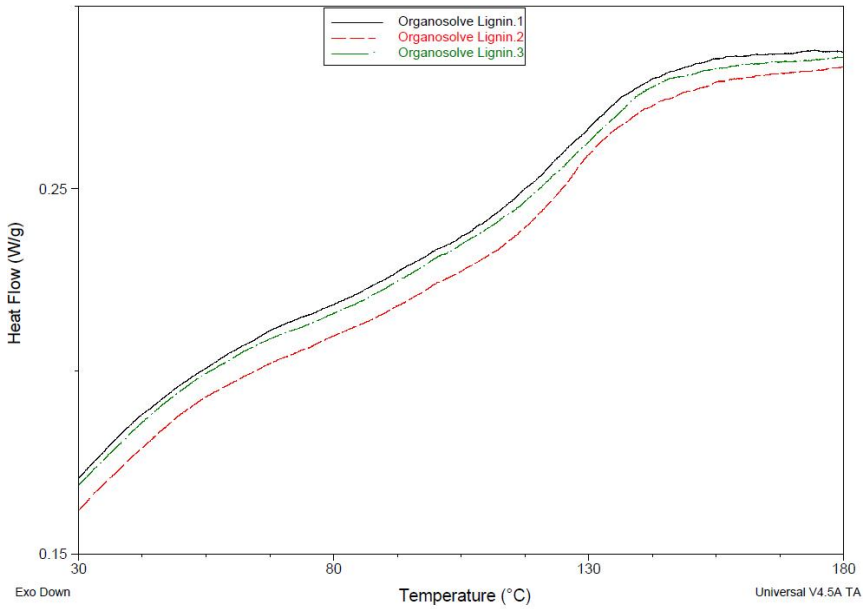

| KLSM Sample | 1 | 2 | 3 |
|---|---|---|---|
| Tg , ℃ | 166 | 166 | 167 |

The average Tg for KLSM sample is about 166 ℃

Indulin AT Tg was found to be 155-157 ℃

# DSC Thermograms for Organosolv Lignin

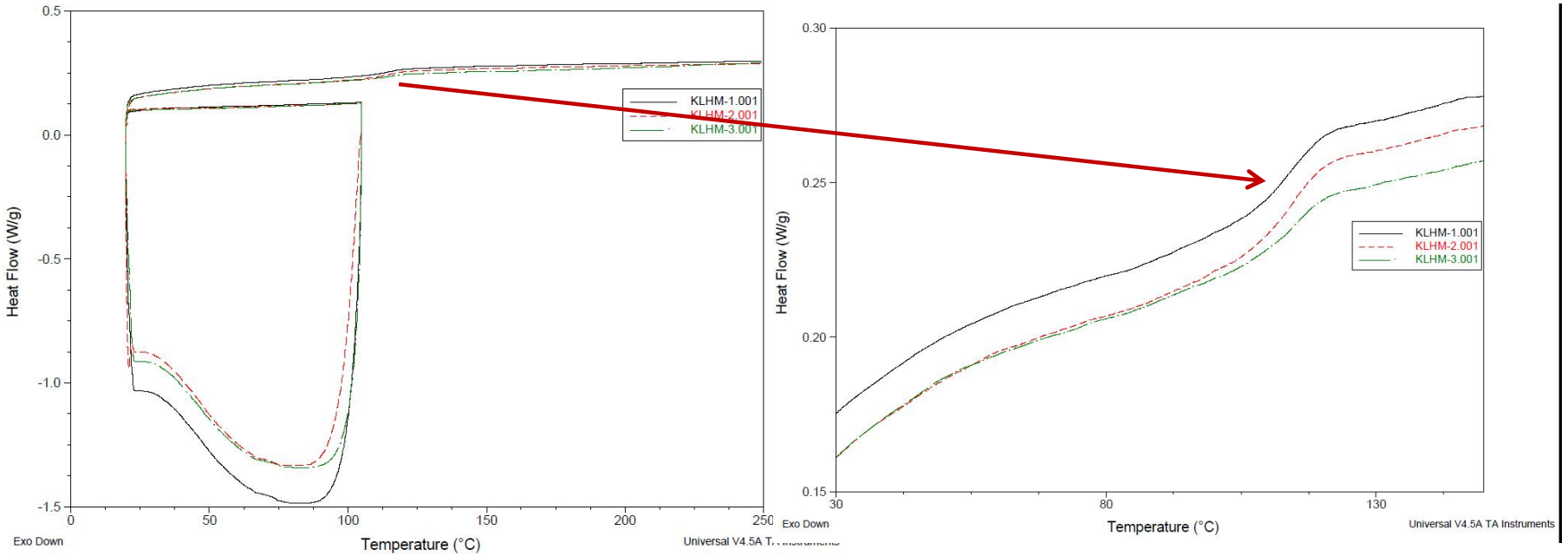



| Test Number | 1 | 2 | 3 |
|---|---|---|---|
| Tg , ℃ | 122 | 124 | 123 |

The average Tg for Organosolv Lignin was about 123 ℃

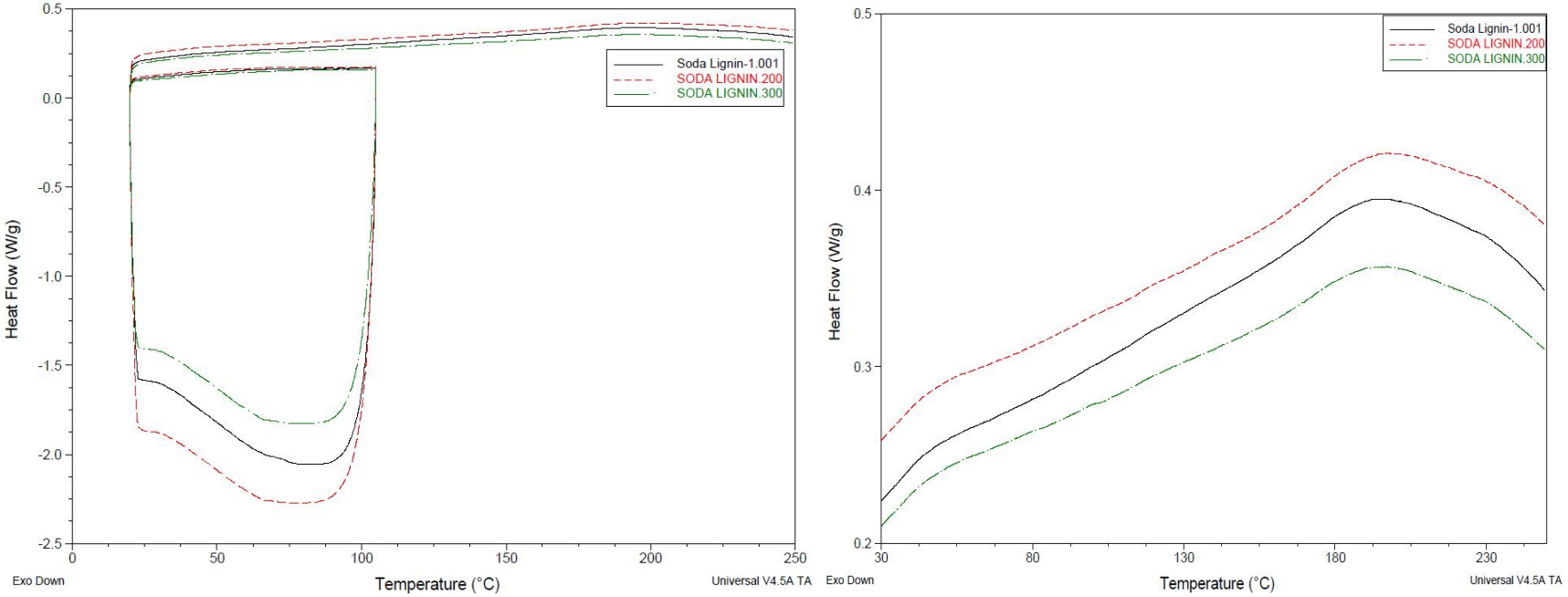
# DSC Thermograms for KLHM Lignin




| Test Number | 1 | 2 | 3 |
|---|---|---|---|
| Tg , ℃ | 112 | 114 | 112 |

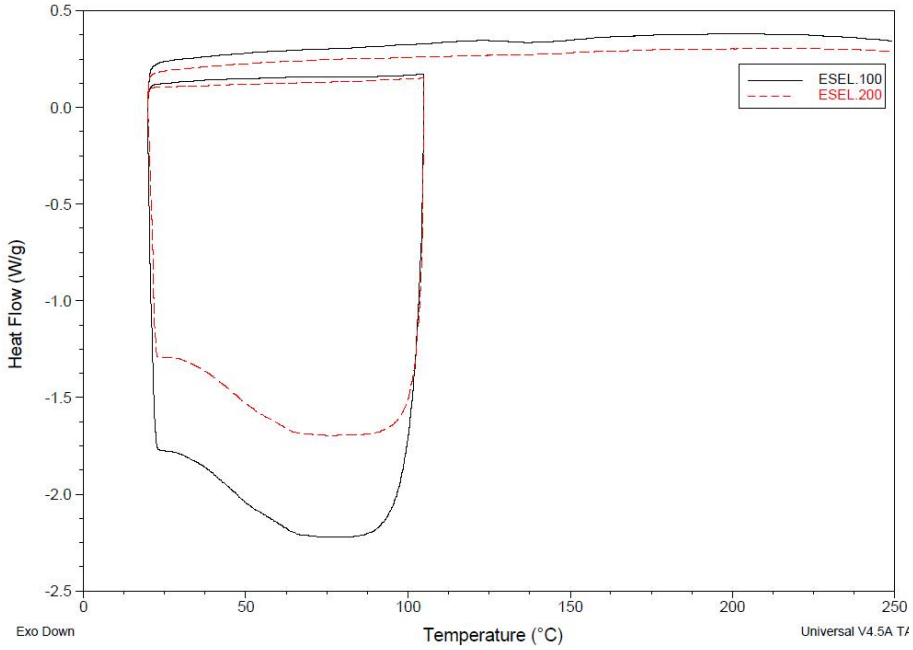
The average Tg for KLHM Sample was about 113 ℃

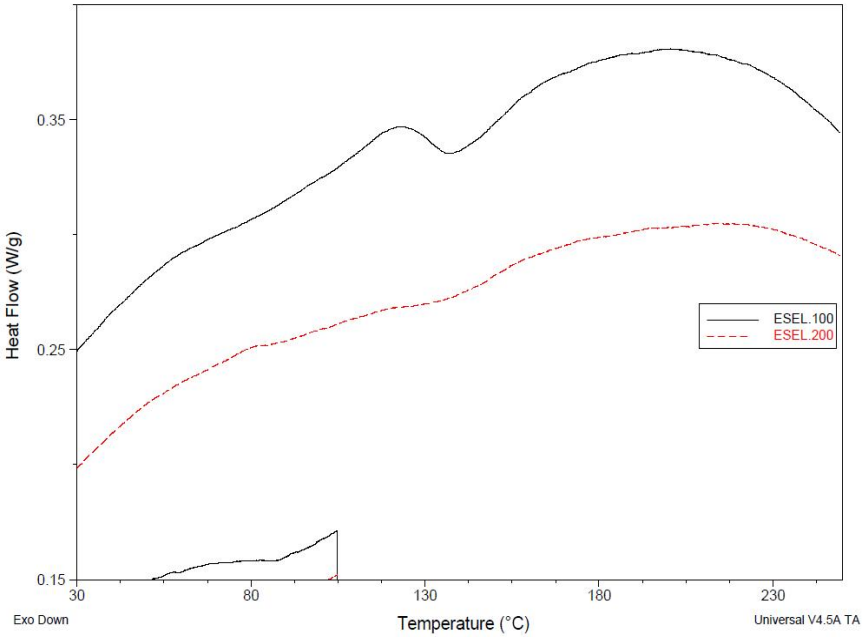
# DSC Thermograms for Soda Lignin




There is no clear Tg for the Soda Lignin sample

# DSC Thermograms for the ESEL Lignin Sample




There is no clear Tg for the ESEL lignin sample