Business from technology

Comparison of the Round Robin method (ADSC) and VTT's in-house method for lignin glass transition analysis

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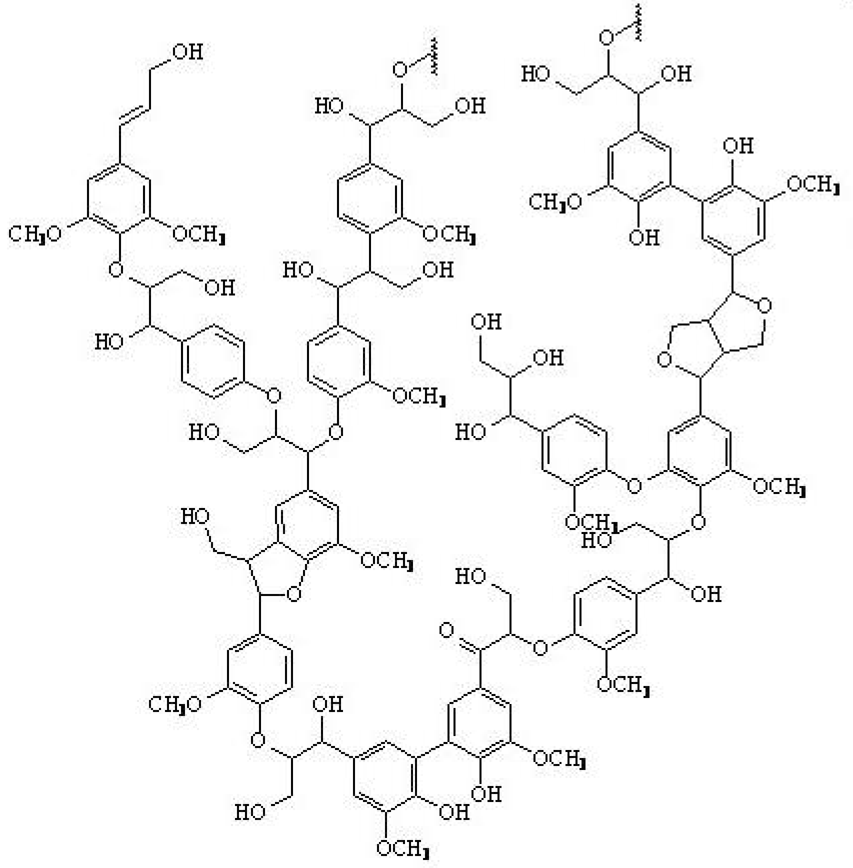
Outline

- Introduction and Motivation
- DSC vs ADSC
- Materials and Methods
- Results
- Conclusions



Introduction

- Lignin is the second most abundant natural polymer
- The random polymeric structure of technical lignins makes it challenging to find applications for their utilization as material
- Depending on the original source and cooking method physico-chemical properties can vary noticeably

  → Affects their suitability to the applications

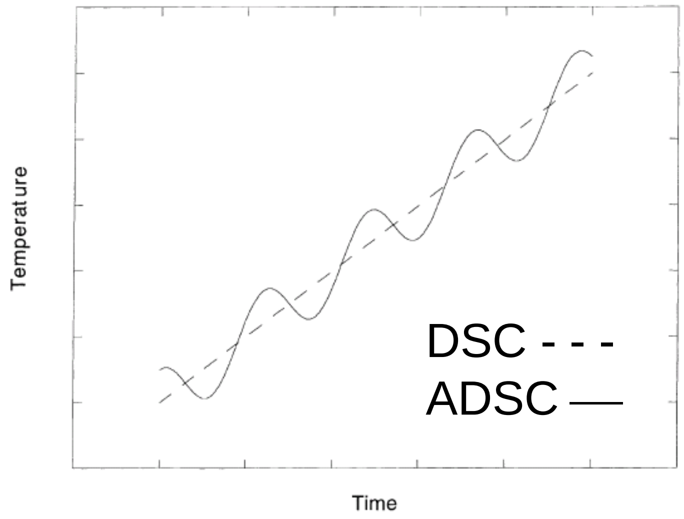
Motivation

- To use all the biomass as effectively as possible
  - $\rightarrow$ Added value from biomass
- To see the effect of thermal treatment to the glass transition temperature (T_g)
  - Compared different cooking method (kraft vs organosolv)
  - Compared wood species (hardwood vs. softwood)

Differential Scanning Calorimetry (DSC)

- DSC is widely used for the characterization of materials with respect to state (Tg) and phase (Tc, Tm) transitions.
- **Glass Transition (Tg)** is an endothermic event, a change in heat capacity that is depicted by a shift in the baseline. It is considered the softening point of the material.
- In the conventional DSC a constant heating rate is used.
- In the alternating DSC (ADSC) a periodic temperature modulation is used.
- Usually, the conventional DSC measurement is used to determine the suitable temperature region for ADSC measurement.

Heat Capacity (Cp) is the amount of heat required to raise a unit mass of a material one degree in temperature.
$Cp = Q/m\Delta T$,
where: Cp = specific heat, Q = heat added, m = mass of material, ΔT = change in temperature.



Pros and cons of the conventional DSC and ADSC techniques

Conventional DSC

Pros

- **Fast compared to ADSC**
- A few measurement parameters

Cons

- Overlapping transitions disturb the characterization
- Sensitivity to small transitions is limited
- Calculation of crystallinity is often wrong

ADSC (alternating DSC)

Pros

- Multiple signals are recorded in one experiment -> **overlapping transitions can be separated** (thermodynamic and kinetic response)
- Heat capacity and heat flow measured at once

Cons

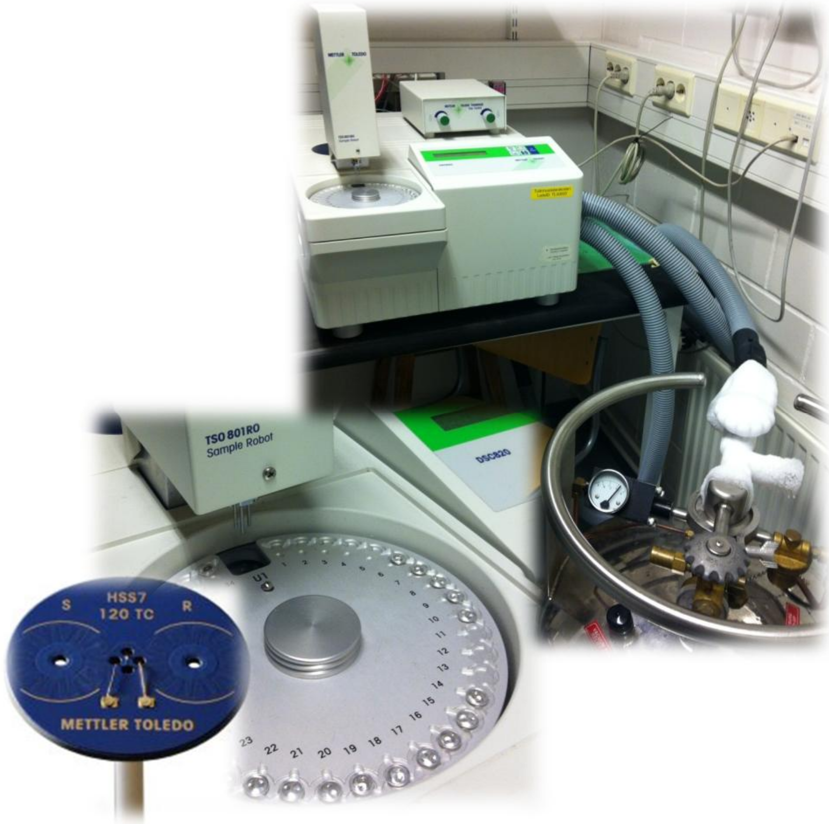
- Slow compared to conventional DSC
- Requires several measurement parameters → optimization

Materials

Code	Lignin sample
KLHM	Hardwood LignoBoost kraft lignin
KLSM	Softwood LignoBoost kraft lignin
SprOrgS	Spruce organosolv lignin
ESEL	Enzymatically treated steam explosion poplar lignin
Soda	Soda lignin from wheat

Instrument

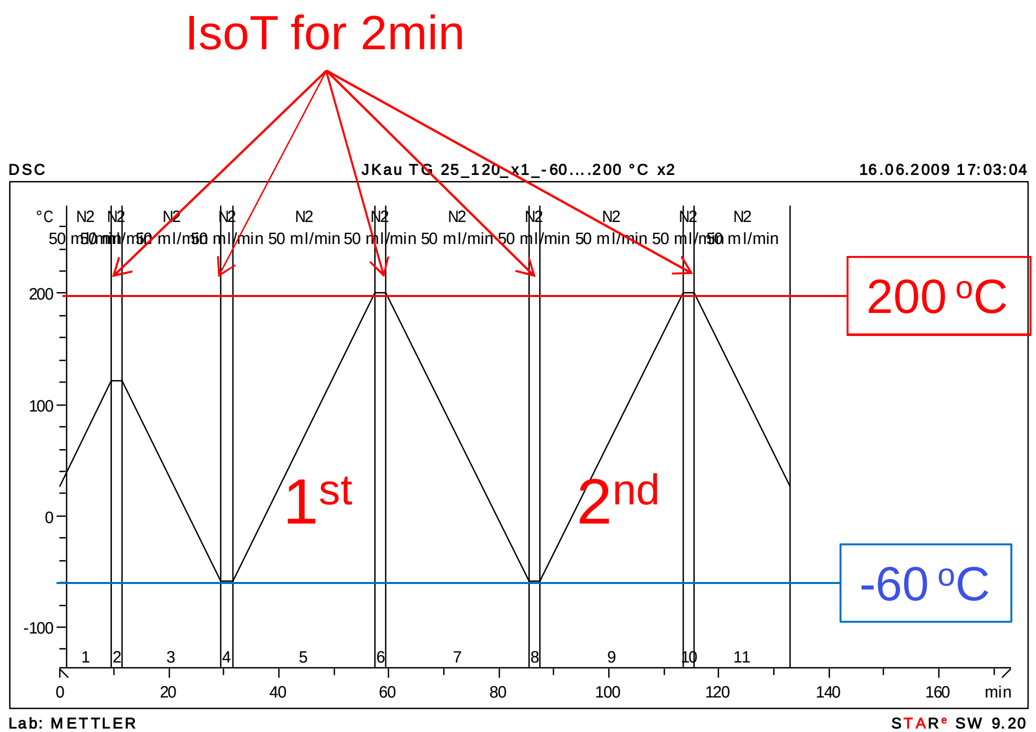
- Mettler Toledo Differential Scanning Calorimeter (with ADSC option) model DSC820 system STARe SW 9.20, Mettler Toledo GmbH, Switzerland
- 40 μl sealed aluminium crucibles, pre-treated at 500 ºC to oxidize the surface



Testing method: VTT's in-house

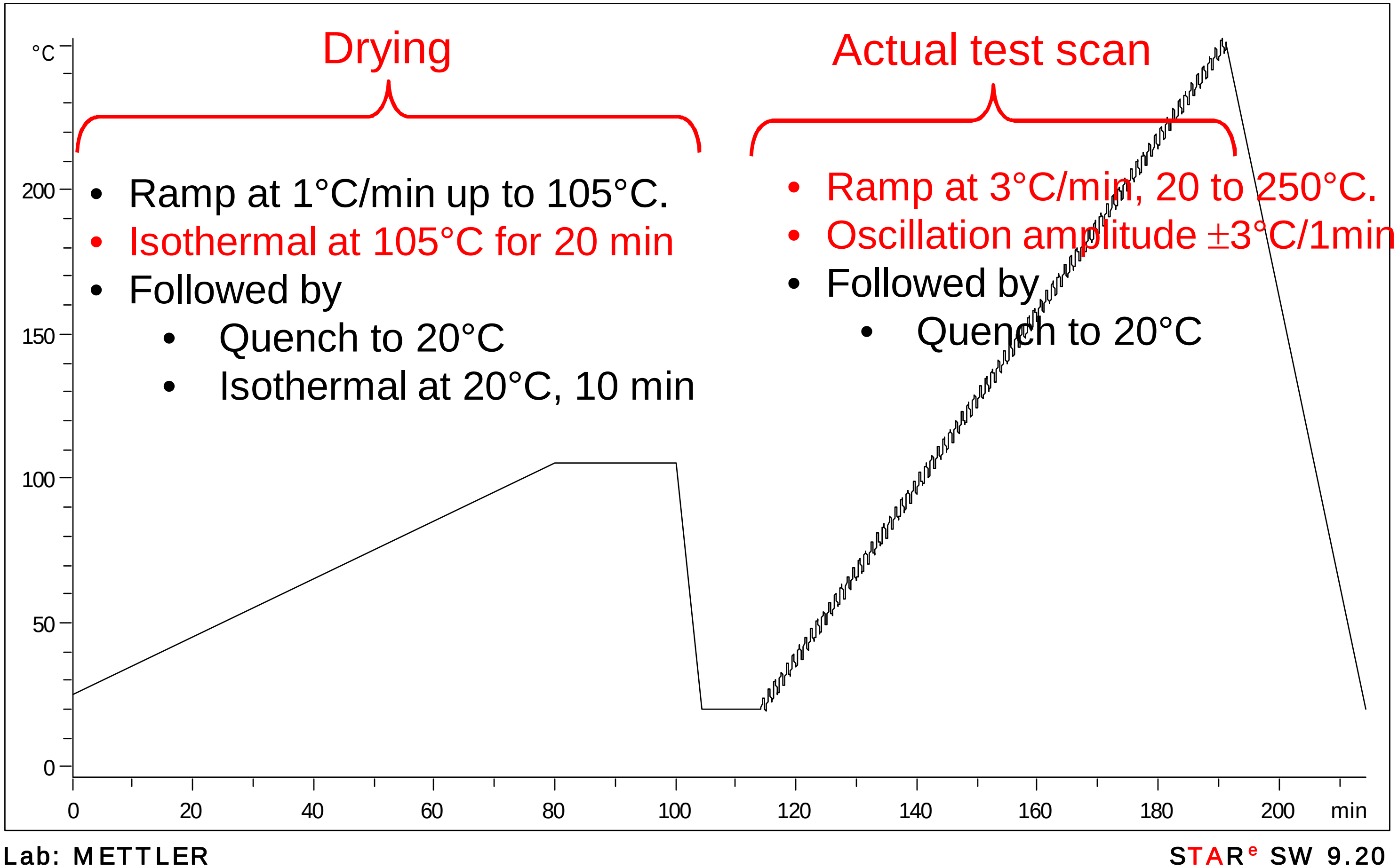
- **Method**
  - Heating and cooling (LN_2) 10 °C/min
  - N_2 flow 50 ml/min
  - Sample 6 to 10 mg

1. Dynamic phase from 25 ºC to 120 ºC
2. Isothermic phase at 120 ºC, 2 min (**Drying**)
3. Dynamic phase from 120 ºC to -60 ºC
4. Isothermic phase at -60 ºC, 2 min
5. **Dynamic phase from -60 ºC to 200 ºC (1st heating)**
6. Isothermic phase at 200 ºC, 2 min
7. Dynamic phase from 200 ºC to -60 ºC
8. Isothermic phase at -60 ºC, 2 min
9. **Dynamic phase from -60 ºC to 200 ºC (2nd heating)**
10. Isothermic phase at 200 °C, 2 min
11. Dynamic phase from 200 °C to 25 °C

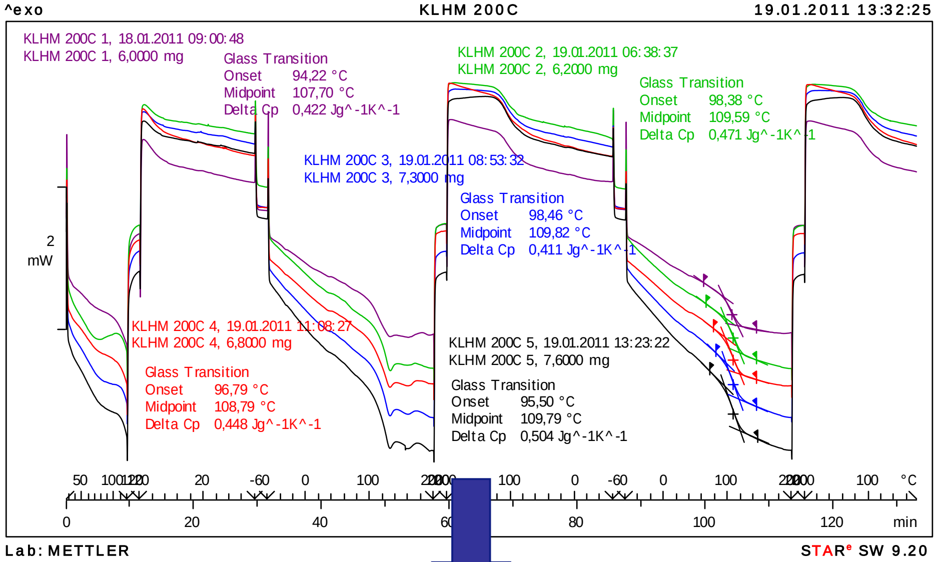


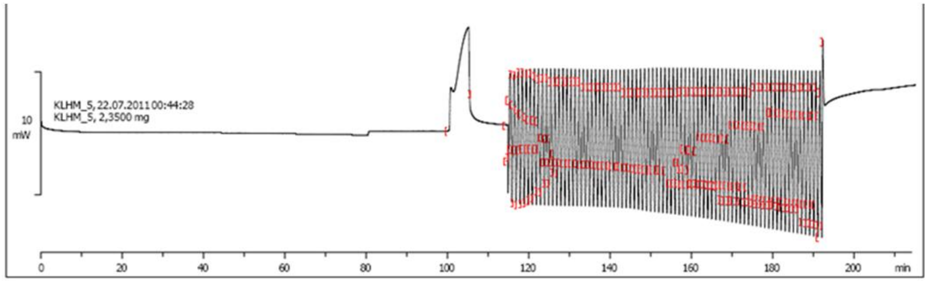
Testing method: Round Robin ADSC

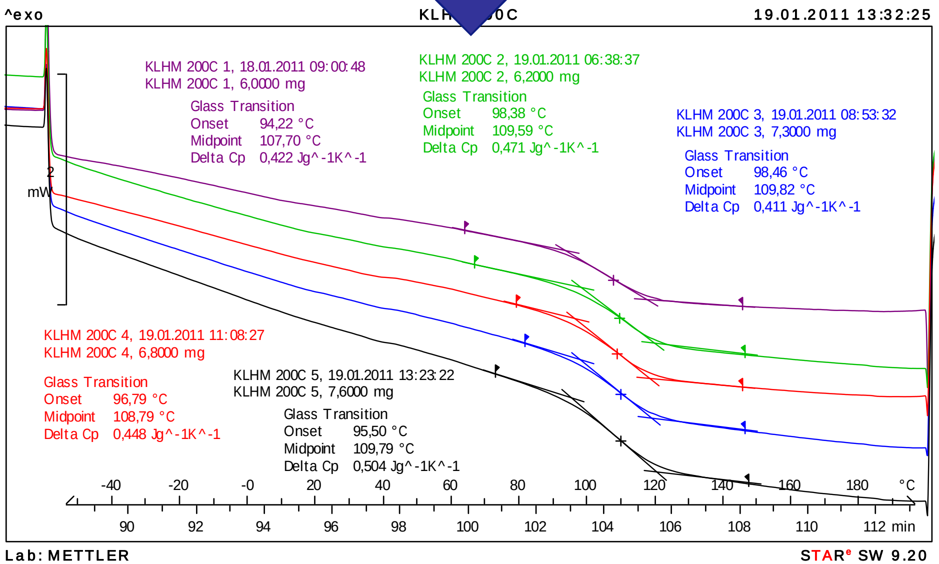
- N_2 flow 50 ml/min
- Sample 1 to 2 mg

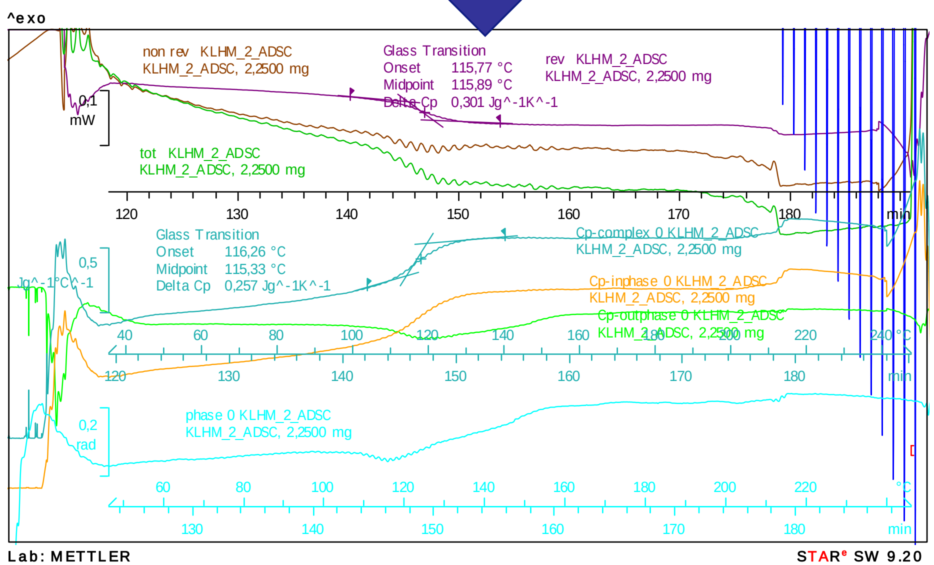


Conventional DSC vs. ADSC









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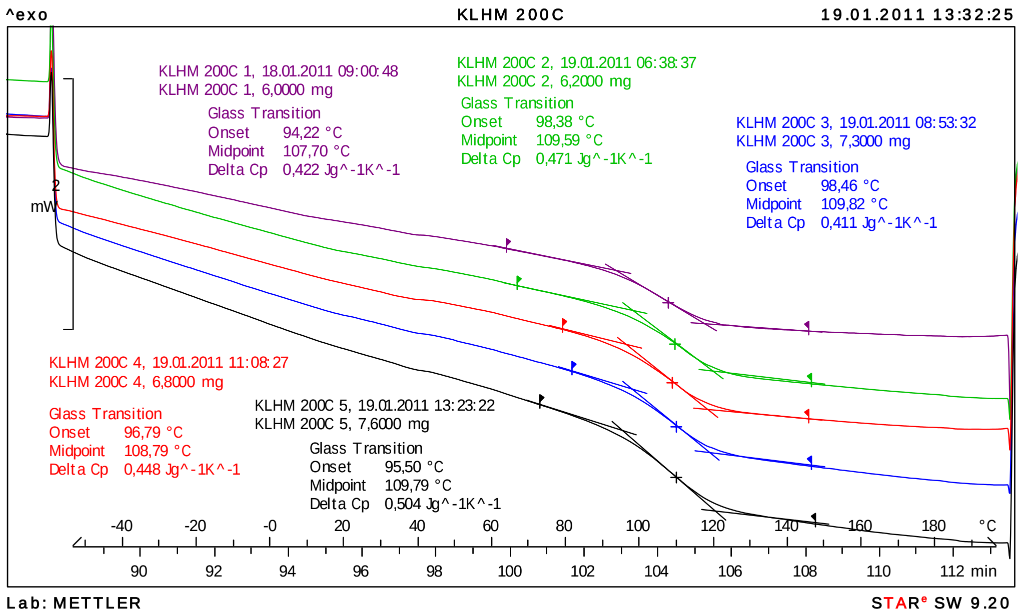
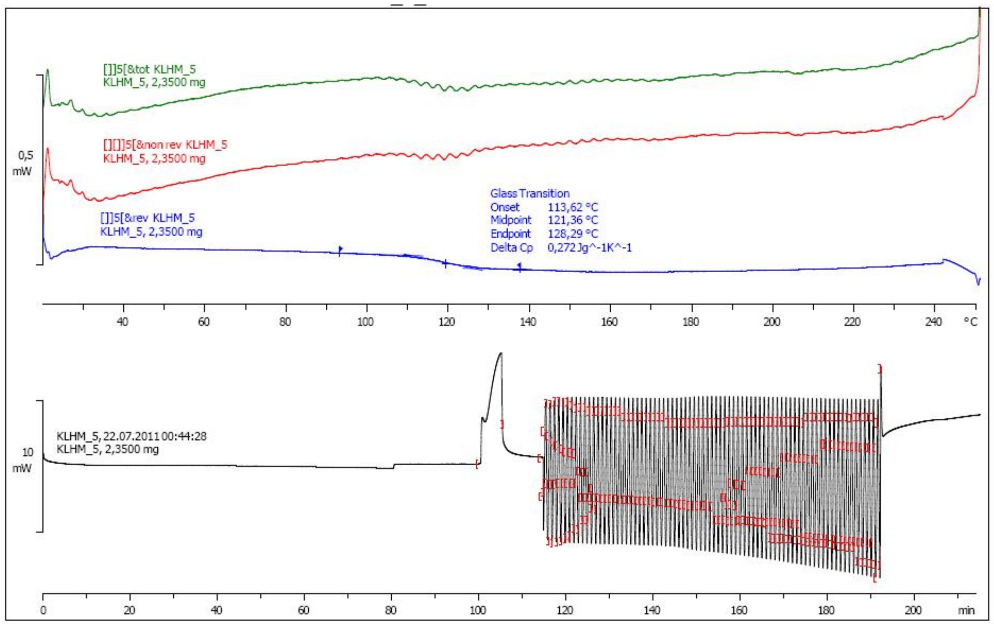
KLHM by DSC and ADSC

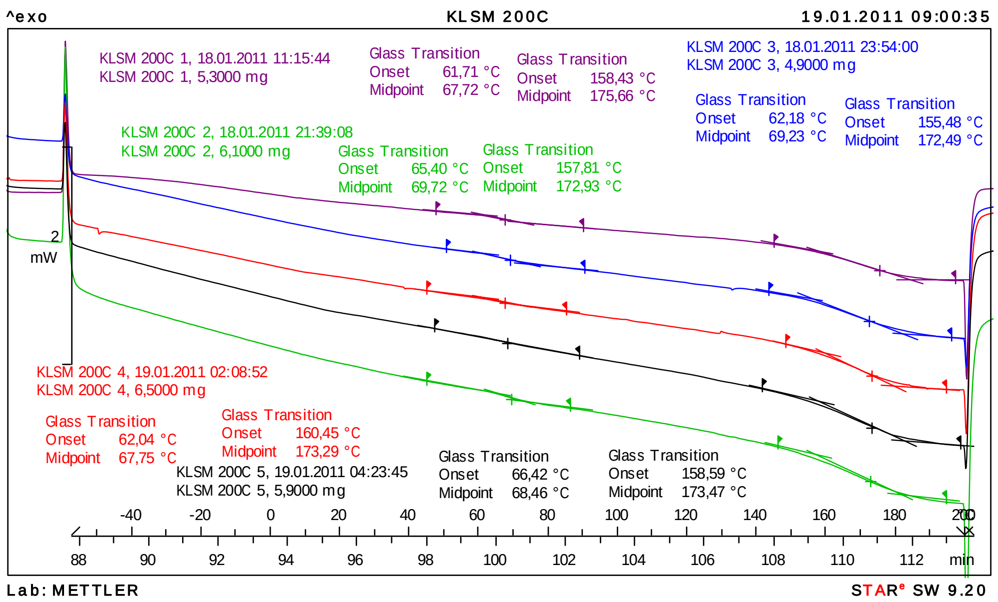


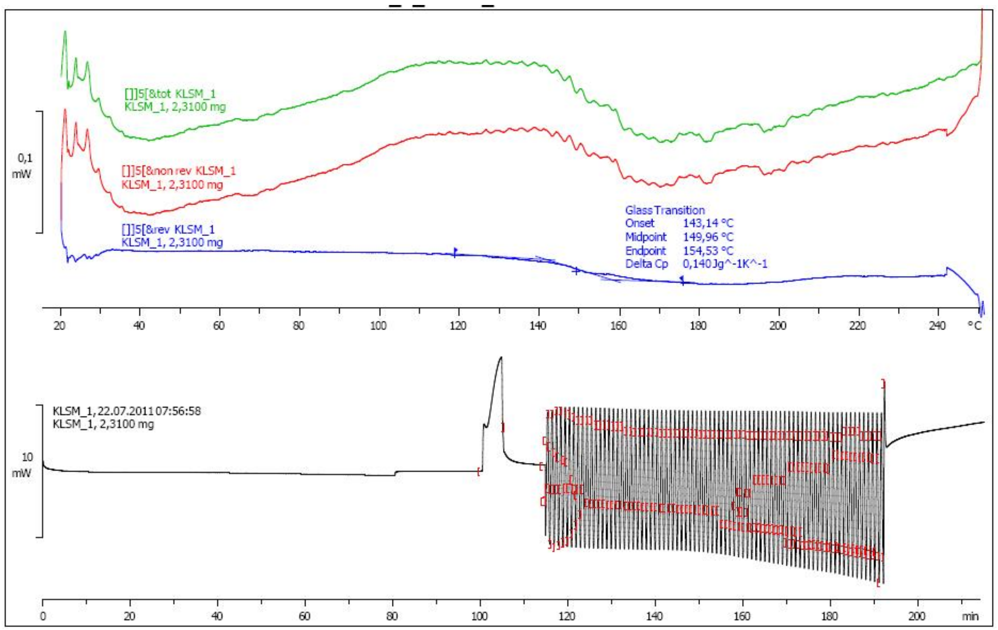


Tg 109 ± 1

Tg 116 ± 1

KLSM by DSC and ADSC

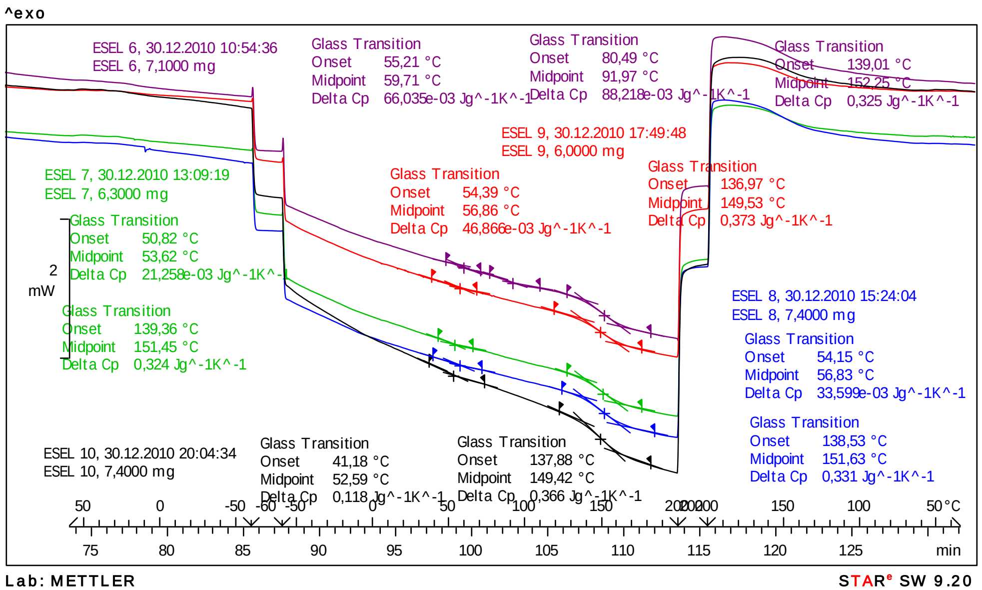


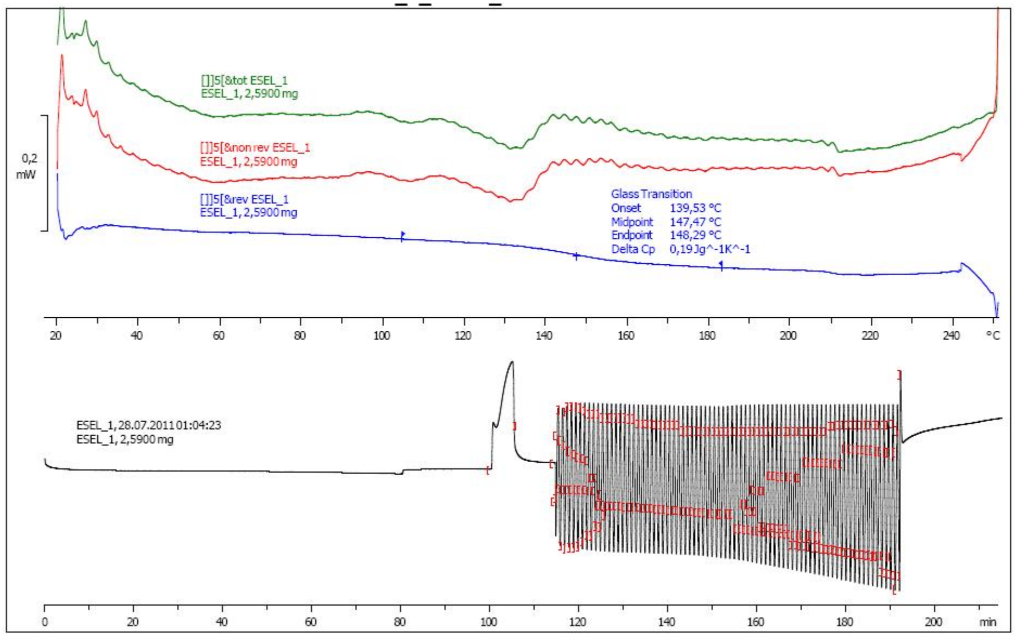


Tg 174 ± 1

Tg 155 ± 6

ESEL by DSC and ADSC

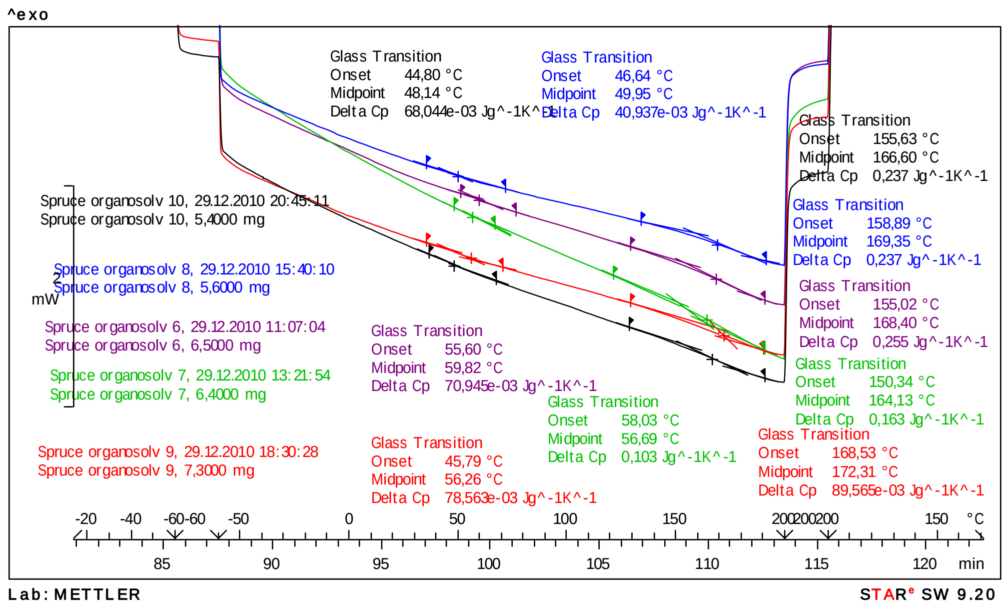


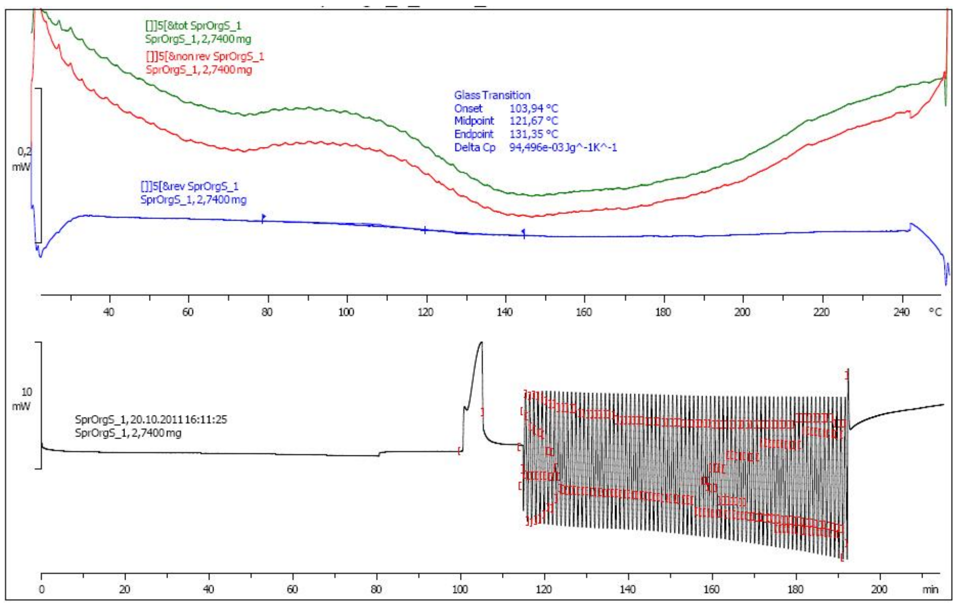


Tg 151 ± 1

Tg 146 ± 3

SprOrgS by DSC and ADSC

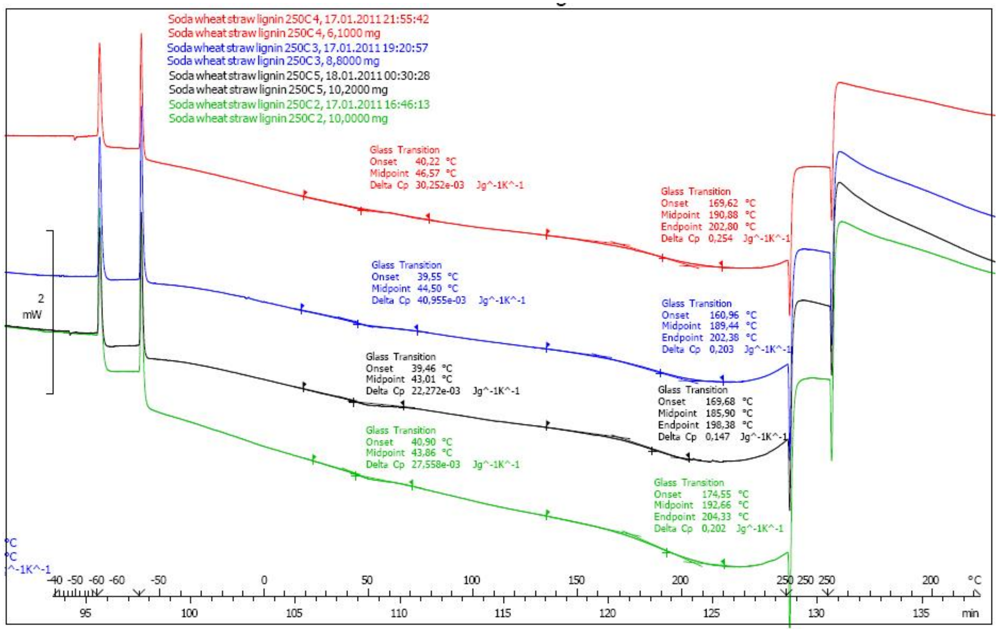


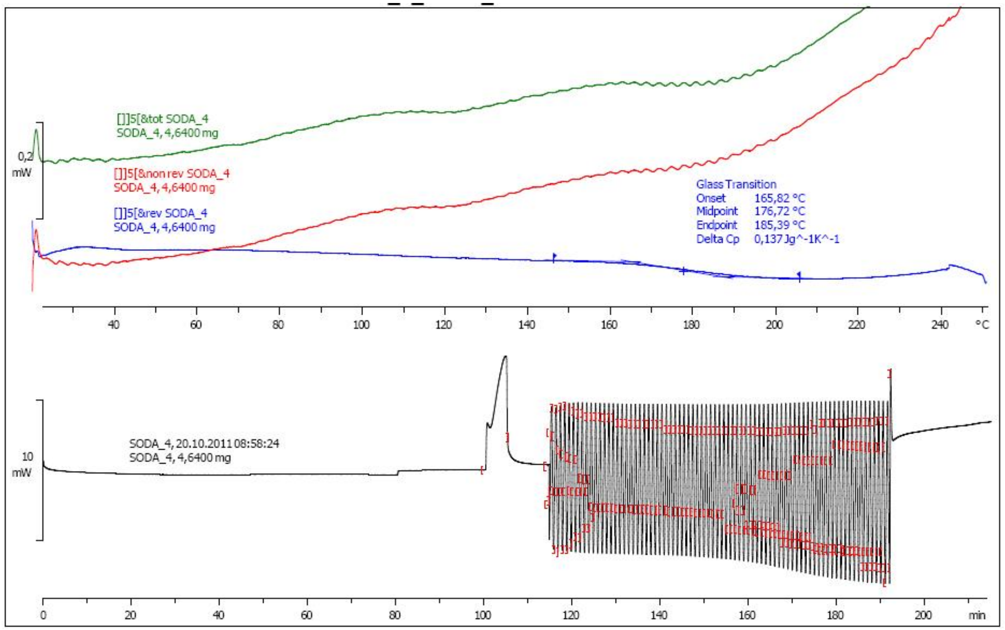


Tg 168 ± 3

Tg 114 ± 11

Soda by DSC and ADSC





Tg 190 ± 3

Tg 145 ± 22

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Glass transition by VTT's in-house vs Round Robin methos

	VTT's in-house		Round Robin	
	DSC Tg (°C, mid)	ΔCp ($J\ g^{-1}\ K^{-1}$)	ADSC, rev. Tg (°C, mid)	ΔCp ($J\ g^{-1}\ K^{-1}$)
KLHM	109 ± 1	0.451 ± 0.038	116 ± 1	0.321 ± 0.115
KLSM	174 ± 1	0.342 ± 0.052	155 ± 6	0.144 ± 0.029
ESEL	151 ± 1	0.344 ± 0.024	146 ± 3	0.267 ± 0.054
SprOrgS	168 ± 3	0.196 ± 0.096	114 ± 11	0.092 ± 0.092
Soda	190 ± 3	0.202 ± 0.044	145 ± 22	0.209 ± 0.204

Average and S.D. values from 3 to 5 samples

Conclusions

- The conventional and alternating DSC experiments were carried out for the lignin samples.
- In the present study the conventional DSC (VTT's in-house method) showed better repeatability for Tg than Round Robin ADSC method.
- Generally, VTT's in-house method showed Tg at higher temperature than Round Robin ADSC method.

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