COST Action FP0901
Round Robins of lignin samples
Part 2: Thermal properties

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1 Summary

The intention of this Round Robin test was to settle common methods for isolated lignins for determination of the most fundamental thermal characteristics; T_g and decomposition temperature (T_d). Five lignin samples were used; kraft lignin from birch/aspen wood and pine/spruce, respectively, organosolv spruce lignin, soda wheat straw lignin and enzymatic treated steam explosion poplar wood lignin. The samples thus represent different raw materials and types of processing of interest in today's research and development. The samples were analysed with respect to common impurities and fundamental properties.

Nine laboratories participated in part or in all thermal analysis. The T_d was analysed by six-seven laboratories using a distributed Innventia method. For the T_g determination six of the laboratories used an Innventia method and three used their in-house methods.

For the determination of the T_d, good reproducibility between the laboratories was observed irrespective of the lignin sample type and purity.

The determination of the glass transition temperature (T_g), was more difficult for lignin samples containing large amounts of non-lignin components such as high ash content and/or high carbohydrate content. Eventual residues from proteins did not appear to obstruct the T_g (or the T_d) analysis. Consequently the best agreement between the laboratories for the T_g determination were for the two kraft lignin samples and the lignin sample obtained from enzymatic hydrolysis of steam explosion lignin. A large scatter in the data was obtained for the organosolv and soda lignin samples, respectively. A common observation was that the scatter in the T_g values was considerably less when the common (Innventia) method was used as compared to when all results were included.

Only two laboratories compared their In-house methods with the distributed Innventia method. No systematic difference could be observed between the two methods, but since one of the series represents single measurements, no real conclusions can be drawn from this part of the Round Robin. Thus, the importance of a certain method on the obtained T_g value remains to be settled.

2 Introduction

Isolated lignins are potential value-added products for the industry. Different methods and evaluation procedures are used worldwide for characterization of lignins and especially the thermal properties is of increased importance. One of the most frequently used properties in this context is the glass transition temperature (T_g) which is the temperature at which an amorphous polymeric material undergoes a reversible transition from a hard solid state to a more rubbery state. The change between the two is observed in a broad temperature range, and the specific T_g is determined by convention either as the on-set temperature or as the middle point of the temperature range. The most commonly analytical methods used today is differential scanning calorimetry (DSC). The method used may also differ in the conditions such as drying cycles and different heating rates. The reported T_g values do not only depend on the sample properties, but also on the applied procedure.

The intention of this Round Robin test was to settle common methods for isolated lignins for determination of the most fundamental thermal characteristics; T_g and decomposition temperature (T_d). The specific questions to be answered were if the same method can be used irrespective lignin sample type and if different analytical protocols influence the measured values.

3 Experimental

3.1 Samples

Five lignin samples were collected and used in this Round Robin, see Table 1. In the following, the samples are referred to according to respective designations.

Table 1. An overview of samples used in this study, as well as designations, sources and supplying laboratories.

Sample	Sample designation	Raw material sources	Supplying laboratory
Hardwood kraft lignin	KLHM	birch/aspen	Innventia, Sweden
Softwood kraft lignin	KLSM	pine/spruce	Innventia
Organosolv lignin	Orgsolv	spruce	VTT, Finland
Soda lignin	Soda	wheat straw	WUR, the Netherlands
Enzymatic treated steam explosion lignin	ESEL	poplar	vTi, Germany

3.2 Fundamental characteristics

The lignin content and characteristics of the samples were determined at Innventia using standard methods. The total lignin is the combined amount of Klason lignin and acid insoluble lignin and the carbohydrate content was determined after acid hydrolysis. The ash content was determined after combustion at 525°C. The molecular mass characteristics were determined on acetylated samples in THF-SEC system, relative polystyrene.

3.3 Thermal analysis – T_d determination

The following Innventia method (Nordström et al. 2012) was distributed to the participating laboratories. Details of deviation from this procedure as well as instrumental information at participating laboratories are found in the attachments of this report.

The same sample size as for DSC analysis (see 3.4.1 below) was used. Prior to measurement, the sample was dried at 105°C for 20 min, before quenching to room temperature. The analysis was done by increasing the temperature to 350°C while recording the mass loss. The reported T_d, was defined as the temperature where 95% of the initial dry sample remained.

3.4 Thermal analysis – T_g determination

The following Innventia method (Nordström et al. 2012) was distributed to the participating laboratories. Details of deviation from this procedure, use of any in-house method as well as instrumental information at participating laboratories are found in the attachments of this report.

3.4.1 Sample preparation

A sample of 1-3 mg of lignin sample is placed in a hermetic aluminum pan. The pans used at Innventia have a diameter of ~5mm, if different the sample size should be adapted to the pan size, but the lignin powder should cover the bottom of the pan. A hole is produced by piercing the lid with a pair of tweezers (Ø ~0.5mm). The sample should cover the bottom of the pan to ensure good contact. The sample is weighed after piercing of the lid. The method used at Innventia is modulated reversed calorimetry where the temperature is increased by oscillation of ±3°C every 60 seconds. The analysis was performed with TA Instrument Q1000 at Innventia.

3.4.2 Drying and test cycle

The drying cycle was done by increasing the temperature for 1°C/min to 105°C where it was isothermally exposed for 20 min before quenched to 20°C, where it was held for 10 min. The test cycle started directly thereafter by increasing the temperature by 3°C/min to 250°C.

3.4.3 Evaluation

Reported T_g was defined as the inflection point of the heat capacity-temperature curve. The software used at Innventia was Universal analysis 2000 (version 4.5A).

4 Results and discussion

4.1 The lignin samples

The five lignin samples were selected to represent different raw materials and types of processing of interest in today's research & development. Initially the collected samples were analysed with respect to common impurities and fundamental properties, see Table 2.

Table 2. A summary of the sample characteristics of the samples used in this study.

Sample	Total lignin (%)	Carbo-hydrates (%)	Ash (%)	M_w	M_n	PD (M_w/M_n)
KLHM	96.0	1.5	0.7	3300	900	3.7
KLSM	95.7	1.2	0.8	7000	1400	4.9
Orgsolv	80.9	3.0	3.6	2300	600	3.7
Soda	72.5	13.3	10.6	6200	2100	2.9
ESEL	87.4	0.9	2.9	7100	1300	5.6

As expected, all samples contained high amounts of lignin, especially the two kraft lignins. The Soda sample was least pure and contained large portions of carbohydrates as well as inorganics. The lignin, carbohydrates and ash content could explain the major part of the composition of the lignin samples. However, 12.5% of the Orgsolv sample and 9.2% of the ESEL sample still remains to be identified. It can be assumed that the unidentified part of the Orgsolv sample may originate from organically bound and/or inorganic phosphorus. The ESEL sample may contain protein (residues), and thus nitrogen analysis could reveal such indicative information. A thorough chemical analysis was however outside the scope of the present Round Robin.

The molecular mass characteristics reveal unusual high values for the KLSM sample. Whereas the corresponding high values for the ESEL sample may be attributed to presence of proteins and the high values for the Soda lignin sample may be due to presence of hemicelluloses, a reason for the high values of the KLSM sample is not clear.

4.2 Thermal analysis

The nine participating laboratories were instructed to initially follow common distributed Round Robin methods the "Innventia methods" (see Experimentals) for T_g and T_d determination, respectively (Nordström et al., 2012), preferentially by multiple analysis (n=5). The latter was however difficult to perform at all laboratories, possibly due to limitation of available resources. Although the main aim was to compare the T_g method, the T_d determination was included because it is more straight forward to

perform and thus the results are expected to deviate less between the labs, besides of being a frequently used thermal analysis.

Eight laboratories contributed to the T_d determination and used the suggested "Innventia method". For the T_g determination six labs used the Innventia method, three labs used in-house methods and two labs used both methods. Some participants reported two T_g values for the same run. In those cases, only the second T_g was used for calculations. The nine participating labs are numbered 1-9 in the following.

4.2.1 Hardwood kraft lignin sample (KLHM)

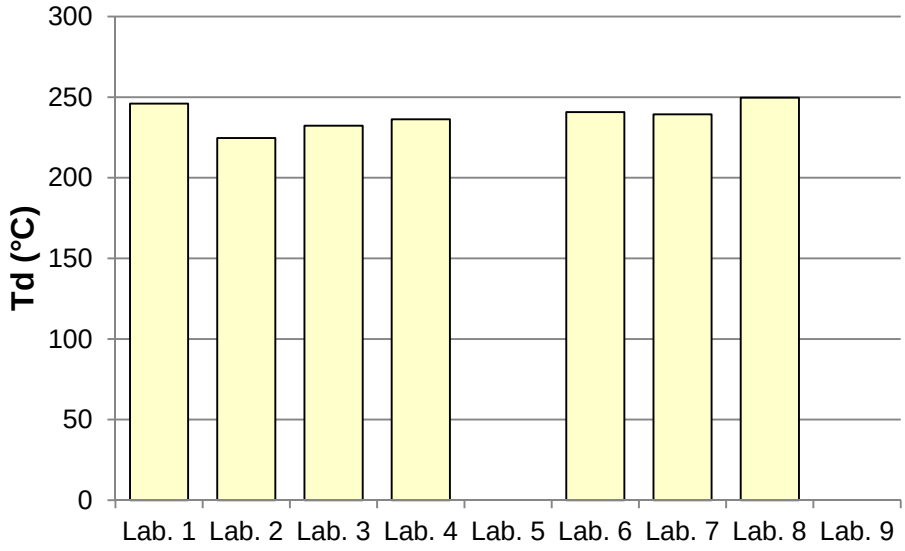

Figure 1. T_d determination of KLHM sample using the distributed Innventia method. Seven of the nine laboratories contributed. Reported values are means of five measurements, except for Lab 1 (n=2).

The in-house methods differed from the distributed Innventia method mainly with respect to heating rate during the test cycle. Lab 3 used 40°C/min; Lab 7 used 10°C/min and Lab 8 used 25°C/min, respectively as compared to the Innventia method 3°C/min. In addition Lab 7 dried the samples for longer times; at 105°C for 16 hours.

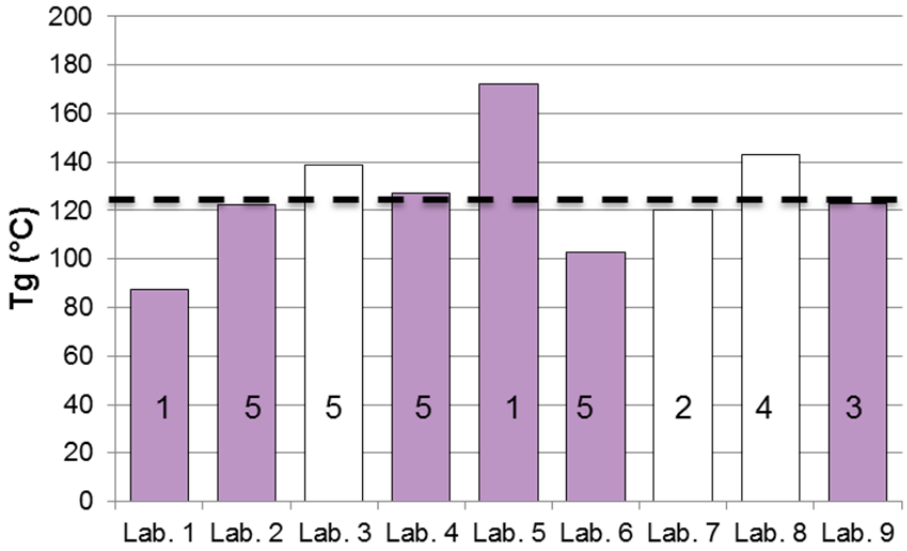

Figure 2. Average of the T_g determination of KLHM sample using the Innventia method (coloured) or a modified Innventia method (white) at participating laboratories (Lab. 1 to 9). The number of measurements (n) is given in the bars. The mean value, 115°C is indicated by the broken line. For details see the Appendices.

4.2.2 Softwood kraft lignin sample (KLSM)

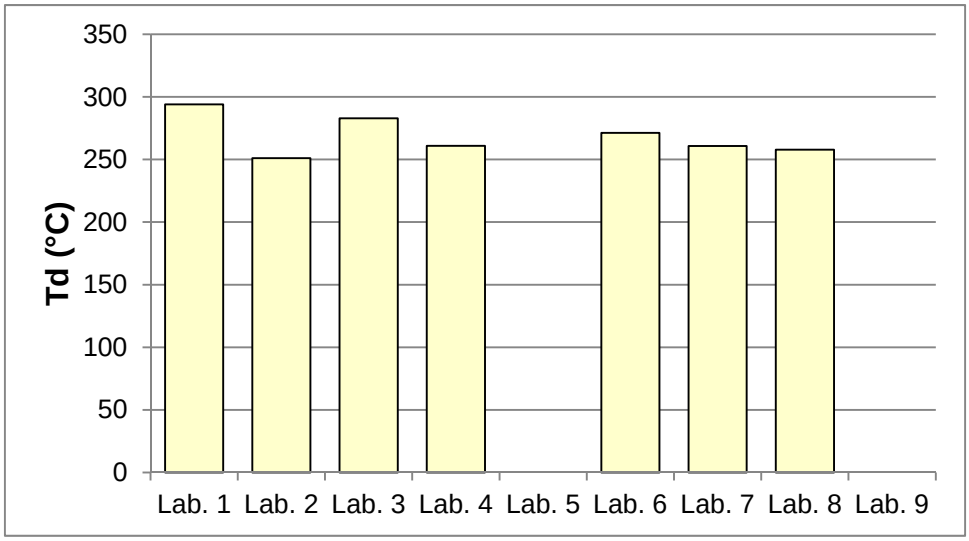

Figure 3. T_d determination of KLSM sample using the Innventia method. Seven of the nine laboratories contributed. The values are means of five measurements (n=5), except for Lab 1 (n=2).

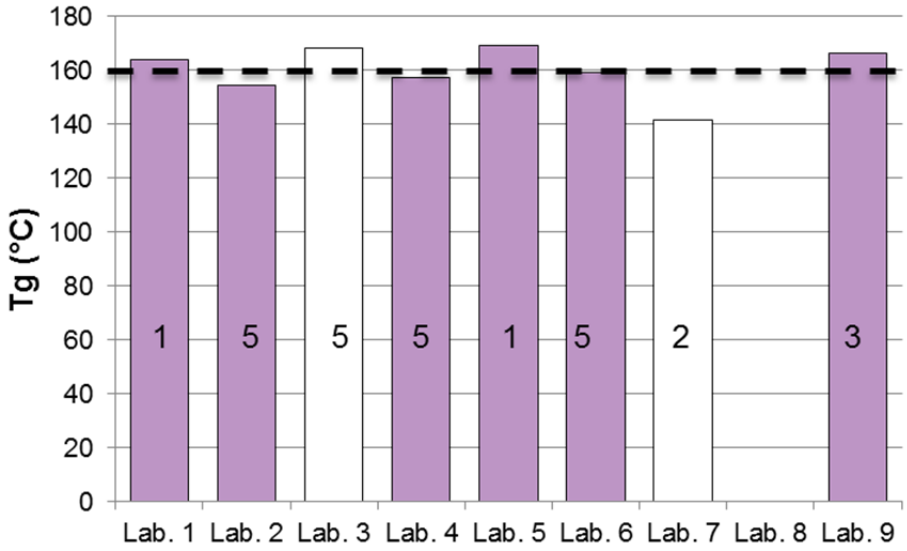

Figure 4. Average of the T_g determination of KLSM sample using the Innventia method (coloured) or a modified Innventia method (white). Eight of the laboratories contributed. The number of measurements (n) is given in the bars. The mean value, 160°C is indicated by the broken line. For details see the Appendices.

4.2.3 Organosolv lignin sample (Orgsolv)

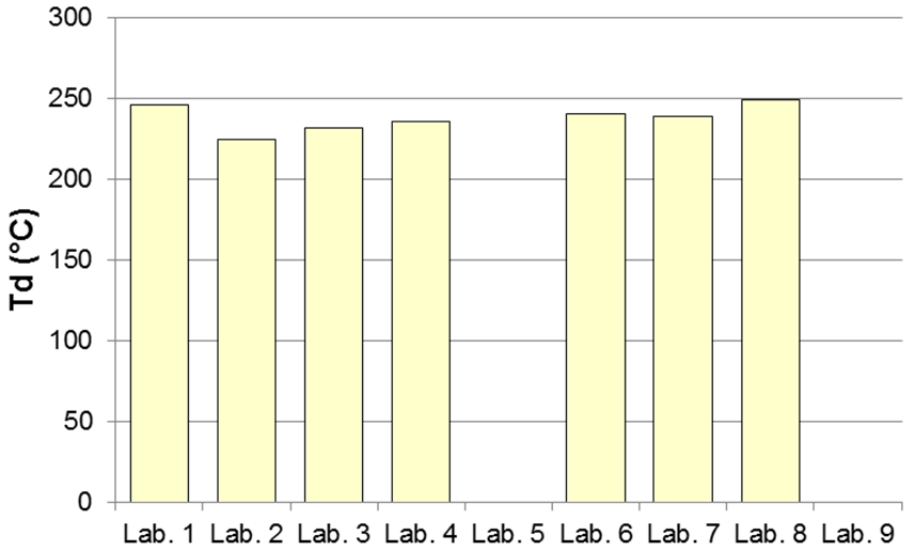

Figure 5. T_d determination of Orgsolv sample using the Innventia method. Seven of the nine laboratories contributed. The values are means of five measurements (n=5), except for Lab 1 (n=2).

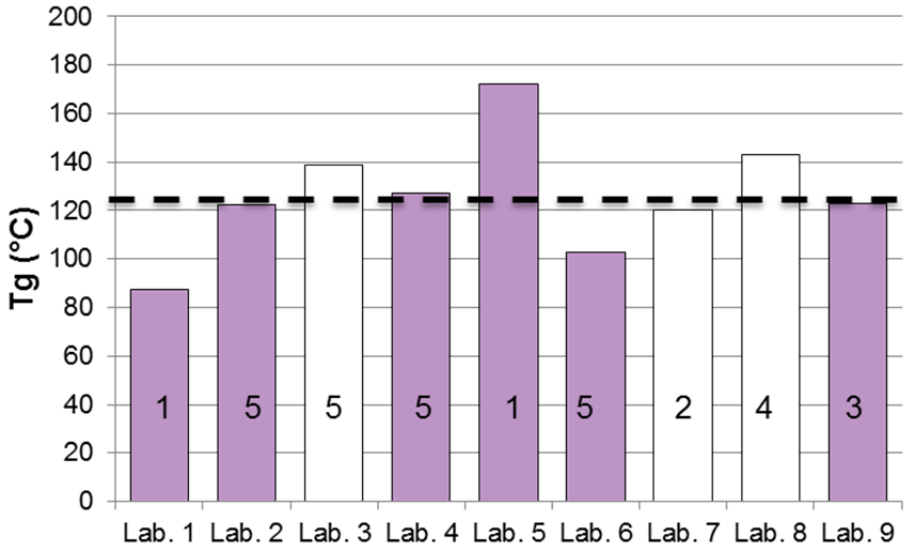

Figure 6. Average of the T_g determination of Orgsolv lignin sample using the Innventia method (coloured) or a modified Innventia method (white). The number of measurements (n) is given in the bars. The mean value, 126°C is indicated by the broken line. For details see the Appendices.

4.2.4 Soda lignin sample (Soda)

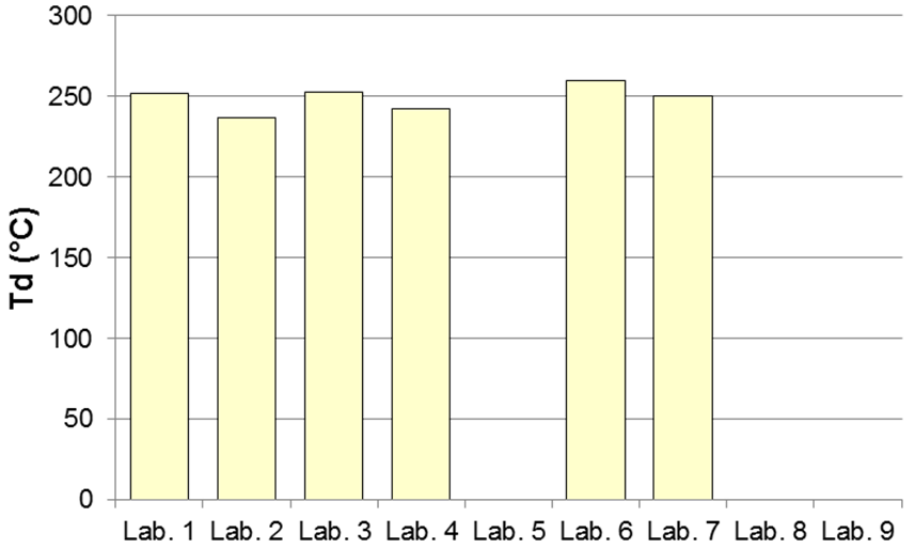

Figure 7. T_d determination of Soda lignin sample using the Innventia method. Six laboratories contributed. The values are means of five measurements (n=5), except for Lab 1 (n=2).

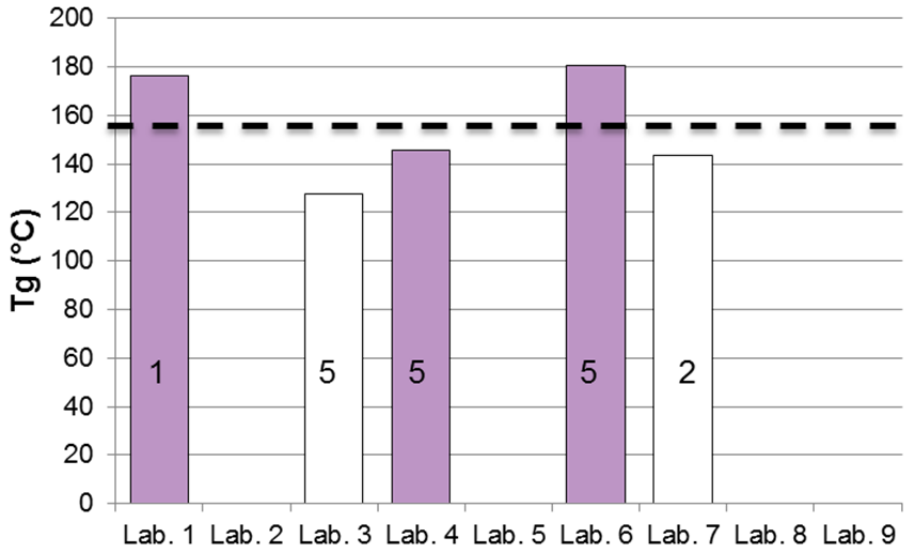

Figure 8. Average of the T_g determination of Soda lignin sample using the Innventia method (coloured) or a modified Innventia method (white). The number of measurements (n) is given in the bars. The mean value, 155 °C is indicated by the broken line. For details see the Appendices.

4.2.5 Enzymatic treated steam explosion lignin sample (ESEL)

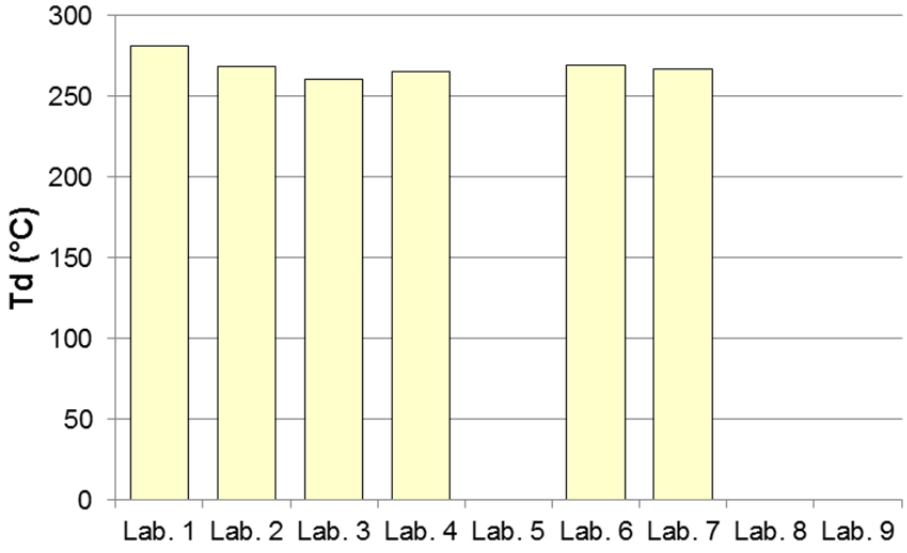

Figure 9. T_d determination of ESEL sample using the Innventia method. Six laboratories contributed. The values are means of five measurements (n=5), except for Lab 1 (n=2).

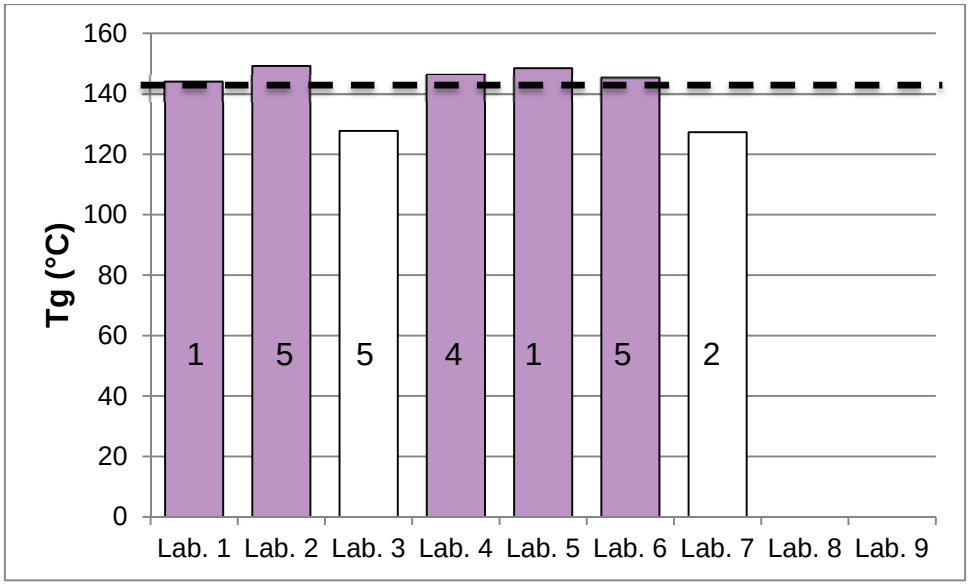

Figure 10. Average of the T_g determination of ESEL sample using the Innventia method (coloured) or a modified Innventia method (white). Seven laboratories contributed. The number of measurements (n) is given in the bars. The mean value, 141 °C is indicated by the broken line. For details see the Appendices.

4.3 Comment on the T_g determinations

The number of measurement differed between the labs, and in addition not all labs used the same method. In the previous compilation all data were included irrespective method used. The T_g determined with a common (the Innventia) method gave (as expected) less scatter in the data between the laboratories, see Table 3, as compared to when the results for the in-house methods were included, see Table 4.

Table 3. Comparison of the average T_g as determined with a common method.

	KLHM	KLSM	OrgSolv	Soda	ESEL
Average T_g, °C	116	162	122	168	147
T_g range, °C	109-122	155-169	88-172	146-180	144-149
T_g difference, °C	13	14	84	35	5

Table 4. Comparison of T_g determined with either a common or an in-house method.

	KLHM	KLSM	OrgSolv	Soda	ESEL
Average T_g, °C	115	160	126	155	141
T_g range, °C	92-123	142-169	88-172	128-180	127-149
T_g difference, °C	32	28	84	53	22

4.4 Determination of T_g – comparison between distributed method and in-house method

Two laboratories analysed the samples both with the Innventia method and with their own in-house method. One of the labs (Lab 1) only made one measurement for each sample and method. The in-house method for Lab 1 deviated from the Innventia method by using a lightly higher amount of sample (5-8 mg as compared to 1-3 mg for the Innventia method). The sample was dried at 110 °C in the aluminium pan (cf. 105 °C for the Innventia method), silicon oil was then added as an antioxidant and to ensure good heat transfer. The test cycle included heating at 10 °C/min (cf. 1 °C/min to 105 °C for the Innventia method). The other in house method (Lab 5) differed from the Innventia method with regard to the in temperature as follows: 25 to 120 °C; 120 to -60 °C, -60 to 200 °C; 200 to -60 °C; -60 to 200 °C using an temperature increase or decrease of 10 °C/min and a hold after each cycle of two minutes. No systematic difference between the two pair of methods could however be observed.

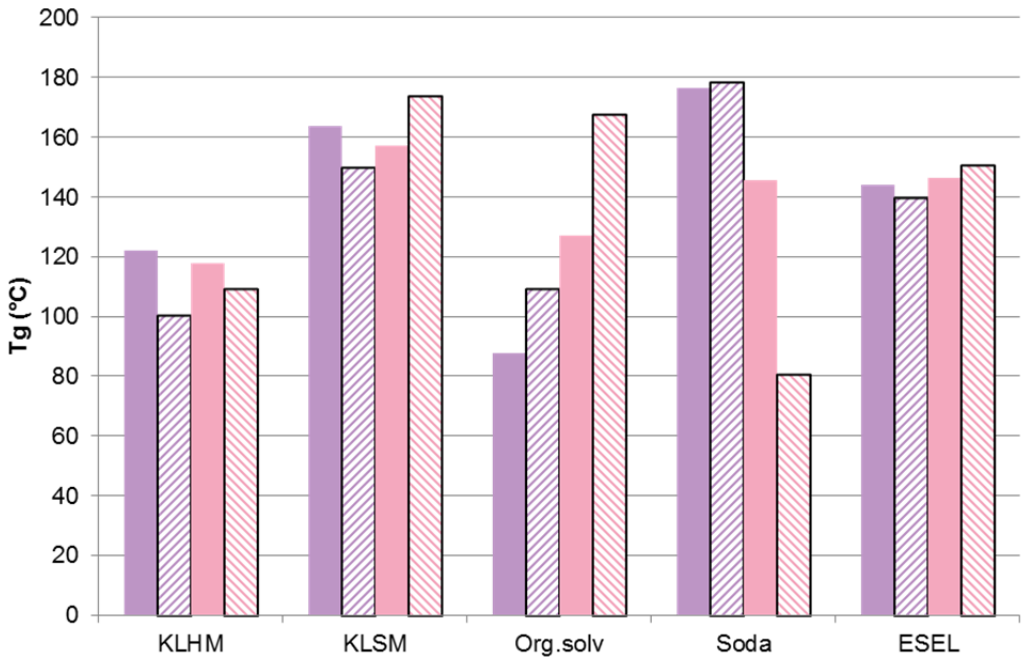

Figure 11. T_g as obtained by the Innventia method (solid) versus In-house method (stripe) at two laboratories. The values from Lab 1 (lilac) is based on one measurement (n=1) and the values from Lab 4 (pink) is based on five measurements (n=5) for all except for the Soda and ESEL sample (n=4).

5 Conclusions

Irrespective of lignin sample type and purity, good reproducibility between laboratories seems to be possible when using the same method for determination of the degradation temperature (T_d) of lignin samples. This conclusion is based on results from 6-7 laboratories.

The determination of the glass transition temperature (T_g), is more difficult for lignin samples containing large amounts of non-lignin components such as high ash content and/or high carbohydrate content. Eventual residues from proteins do not obstruct T_g and T_d analysis, but the contribution from the enzymes to the reported values is not known. Consequently the best agreement between the laboratories was shown for the two kraft lignin samples and the lignin sample obtained from enzymatic hydrolysis of steam explosion lignin.

Only two laboratories compared their In-house methods with the distributed Innventia method. No systematic difference could be observed between the two methods, but since one of the series represents single measurements, no real conclusions can be drawn. Thus, the importance of a certain method on the obtained T_g value remains to be settled.

6 Appendix Lab 1

Lignin	Method	T_g (°C)	T_g (Standard Deviation)	CV (%)	T_g (°C) MV *	Dev. MV (%) **
KLHM	Innventia	122,2	-	-	114.6	6.6
KLSM	Innventia	163,8	-	-	160.0	2.4
Org.solv	Innventia	87,6	-	-	126.3	-30.7
Soda	Innventia	176,3	-	-	154.7	14.0
ESEL	Innventia	143,9	-	-	141.2	1.9

Lignin	Method	T_d (°C)	T_d (Standard Deviation)	CV (%)	T_d (°C) MV *	Dev. MV (%) **
KLHM	Innventia	254,5	-	-	251,3	1,3
KLSM	Innventia	294	-	-	268,4	9,5
Org.solv	Innventia	246	-	-	238,5	3,2
Soda	Innventia	252	-	-	249,1	1,2
ESEL	Innventia	281,5	-	-	268,6	4,8

* Combined mean values (if available the “Innventia-method” was used) for all laboratories.
** Deviation from the combined mean values (+- %).

6.1 Comments

The instruments used for the measurements were Mettler Toledo DSC 12E-differential scanning calorimeter (T_g) and Mettler Toledo TGA/SDTA 851-thermogravimetry analyzer (T_d). Only one or two measurement per sample is available, consequently statistics cannot be calculated. However, plans are to perform additional experiments in the ahead, but at present there are some problems with the instrumentation.

7 Appendix Lab 2

Lignin	Method	T_g (°C)	T_g (Standard Deviation)	CV (%)	T_g (°C) MV *	Dev. MV (%) **
KLHM	Innventia	109.3	0.3	0.3	114.6	-4.7
KLSM	Innventia	154.7	1.2	0.8	160.0	-3.3
Org.solv	Innventia	122.3	1.8	1.5	126.3	-3.2
Soda	Innventia	-	-	-	154.7	
ESEL	Innventia	149.2	2.3	1.6	141.2	5.7

Lignin	Method	T_d (°C)	T_d (Standard Deviation)	CV (%)	T_d (°C) MV *	Dev. MV (%) **
KLHM	Innventia	263.6	0,9	0,3	251,3	4,9
KLSM	Innventia	251.1	0,6	0,3	268,4	-6,4
Org.solv	Innventia	224.7	2,4	1,1	238,5	-5,8
Soda	Innventia	237.0	1,0	0,4	249,1	-4,8
ESEL	Innventia	268.2	0,4	0,1	268,6	-0,1

* Combined mean values (if available the “Innventia-method” was used) for all laboratories.
** Deviation from the combined mean values (+- %).

7.1 Comments by Lab 2

The instruments used for the measurements were Mettler Toledo Star DSC 823-differential scanning calorimeter (T_g) and Mettler Toledo Star System TOA/SDTA 851-thermogravimetry analyzer (T_d). For the “Soda-lignin” no glass transition (inflection) was observed on the heat capacity curve.

8 Appendix Lab 3

Lignin	Method	T_g (°C)	T_g (Standard Deviation)	CV (%)	T_g (°C) MV *	Dev. MV (%) **
KLHM	In-house	119,9	1,1	0,9	114.6	4.6
KLSM	In-house	168,2	4,5	2,7	160.0	5.1
Org.solv	In-house	138,9	1,1	0,8	126.3	9.9
Soda	In-house	127,6	1,7	1,3	154.7	-17,5
ESEL	In-house	127,7	1,6	1,2	141.2	-9,5

Lignin	Method	T_d (°C)	T_d (Standard Deviation)	CV (%)	T_d (°C) MV *	Dev. MV (%) **
KLHM	Innventia	252,0	1,1	0,4	251,3	0,3
KLSM	Innventia	282,9	3,3	1,2	268,4	5,4
Org.solv	Innventia	232,3	1,9	0,8	238,5	-2,6
Soda	Innventia	252,5	1,5	0,6	249,1	1,4
ESEL	Innventia	260,3	1,1	0,4	268,6	-3,1

* Combined mean values (if available the “Innventia-method” was used) for all laboratories.
** Deviation from the combined mean values (+- %).

8.1 Comments

The instruments used for the measurements were Perkin Elmer Pyris 1-differential scanning calorimeter (T_g) and Mettler Toledo M3 TC 15 TA-thermogravimetry analyzer (T_d). Only "in-house" method for T_g-determination was used. The method differs from the "Innventia-method" by the ramp (40 °C/min instead of 3 °C/min). The samples were very challenging to analyse and the final ramp was decided to 40 °C/min as the most suitable.

9 Appendix Lab 4

Lignin	Method	T_g (°C)	T_g (Standard Deviation)	CV (%)	T_g (°C) MV *	Dev. MV (%) **
KLHM	Innventia	117,8	0,9	0,8	114.6	2.8
KLSM	Innventia	157,2	1,2	0,7	160.0	-1.7
Org.solv	Innventia	127,2	2,9	1,7	126.3	0.7
Soda	Innventia	145,8	4,3	5,3	154.7	-5,8
ESEL	Innventia	146,3	1,3	0,9	141.2	3,6

Lignin	Method	T_d (°C)	T_d (Standard Deviation)	CV (%)	T_d (°C) MV *	Dev. MV (%) **
KLHM	Innventia	246,4	2,1	0,9	251,3	-1,9
KLSM	Innventia	260,9	1,8	0,7	268,4	-2,8
Org.solv	Innventia	236,3	3,8	1,6	238,5	-0,9
Soda	Innventia	242,5	2,5	1,0	249,1	-2,6
ESEL	Innventia	265,2	1,1	0,4	268,6	-1,3

* Combined mean values (if available the “Innventia-method” was used) for all laboratories.
** Deviation from the combined mean values (+- %).

9.1 Comments

The instruments used for the measurements were Mettler Toledo Star DSC820-differential scanning calorimeter (T_g) and Seiko Instruments TG/DTA 320-thermogravimetry analyzer (T_d).

10 Appendix Lab 5

Lignin	Method	T_g (°C)	T_g (Standard Deviation)	CV (%)	T_g (°C) MV *	Dev. MV (%) **
KLHM	Innventia	118	-	-	114.6	2.9
KLSM	Innventia	169,2	-	-	160.0	5.8
Org.solv	Innventia	171,9	-	-	126.3	36.1
Soda	Innventia	n.m	-	-	154.7	-
ESEL	Innventia	148,5	-	-	141.2	5,2

Lignin	Method	T_d (°C)	T_d (Standard Deviation)	CV (%)	T_d (°C) MV *	Dev. MV (%) **
KLHM	-	-	-	-	251,3	-
KLSM	-	-	-	-	268,4	-
Org.solv	-	-	-	-	238,5	-
Soda	-	-	-	-	249,1	-
ESEL	-	-	-	-	268,6	-

* Combined mean values (if available the “Innventia-method” was used) for all laboratories.
** Deviation from the combined mean values (+- %).

10.1 Comments

The instrument used for the T_g-measurements were Mettler Toledo Star DSC821-differential scanning calorimeter (T_g) according to the Innventia-method. Only one measurement per sample is available, consequently statistics cannot be calculated. The glass transition temperature increases by repeating the measurements (e.g. condensation reactions) for all lignins. The "first cycle" is therefore used for determination of T_g. No T_d measurements were performed.

11 Appendix Lab 6

Lignin	Method	T_g (°C)	T_g (Standard Deviation)	CV (%)	T_g (°C) MV *	Dev. MV (%) **
KLHM	Innventia	117	0,64	0,5	114.6	2.1
KLSM	Innventia	159	2,33	1,5	160.0	-0.6
Org.solv	Innventia	102,7	0,73	0,7	126.3	-18.7
Soda	Innventia	180,4	4,84	2,7	154,7	16,6
ESEL	Innventia	145,2	1,3	0,9	141,2	2,9

Lignin	Method	T_d (°C)	T_d (Standard Deviation)	CV (%)	T_d (°C) MV *	Dev. MV (%) **
KLHM	Innventia	260	4,4	1,7	251,3	3,5
KLSM	Innventia	271	2,1	0,8	268,4	1,1
Org.solv	Innventia	241	0,9	0,4	238,5	1,0
Soda	Innventia	260	1,6	0,6	249,1	4,4
ESEL	Innventia	269	0,7	0,3	268,6	0,2

* Combined mean values (if available the “Innventia-method” was used) for all laboratories.
** Deviation from the combined mean values (+- %).

11.1 Comments by Lab 6

The instruments used for the measurements were TA Instruments DSC Q1000-differential scanning calorimeter (T_g) and Perkin Elmer TGA7-thermogravimetry analyzer (T_d) according to the Innventia-method.

12 Appendix Lab 7

Lignin	Method	T_g (°C)	T_g (Standard Deviation)	CV (%)	T_g (°C) MV *	Dev. MV (%) **
KLHM	In-house	91,6	-	-	114.6	-20.1
KLSM	In-house	141,5	-	-	160.0	-11.6
Org.solv	In-house	120,4	-	-	126.3	-4.7
Soda	In-house	143,4	-	-	154,7	-7,3
ESEL	In-house	127,3	-	-	141,2	-9,8

Lignin	Method	T_d (°C)	T_d (Standard Deviation)	CV (%)	T_d (°C) MV *	Dev. MV (%) **
KLHM	Innventia	244,3	6,4	2,6	251,3	-2,8
KLSM	Innventia	260,8	5,1	1,9	268,4	-2,8
Org.solv	Innventia	239,4	2,5	1,0	238,5	0,4
Soda	Innventia	250,3	0,8	0,3	249,1	0,5
ESEL	Innventia	267,2	4,4	1,7	268,6	-0,5

* Combined mean values (if available the “Innventia-method” was used) for all laboratories.
** Deviation from the combined mean values (+- %).

12.1 Comments

No information about the brand name and type of instrumentation is available.
The Innventia-method for T_g determination using DSC could not be used due to measurement problems, therefore only the "in-house"-method was used. Only one measurement per sample is useful, consequently statistics cannot be calculated. The "second cycle" is mainly used for T_g. The In-house method differs mainly from Innventia-method by the ramp (10 °C/min instead of 3 °C/min) and that the lignins were dried at 105 °C at 16h prior to the measurement. The T_d was performed according to the Innventia-protocol.

13 Appendix Lab 8

Lignin	Method	T_g (°C)	T_g (Standard Deviation)	CV (%)	T_g (°C) MV *	Dev. MV (%) **
KLHM	In-house	123.3	1.0	0.8	114.6	7.5
KLSM	In-house	-	-	-	160.0	
Org.solv	In-house	143.1	3.2	2.2	126.3	13.2
Soda	In-house	-	-	-	154.7	-
ESEL	In-house	-	-	-	141.2	-

Lignin	Method	T_d (°C)	T_d (Standard Deviation)	CV (%)	T_d (°C) MV *	Dev. MV (%) **
KLHM	Innventia	238.0	4.9	2.1	251.3	-5.3
KLSM	Innventia	257.8	1.4	0.6	268.4	-3.9
Org.solv	Innventia	249.7	5.5	2.2	238.5	4.7
Soda	Innventia	-	-	-	249.1	-
ESEL	Innventia	-	-	-	268.6	-

* Combined mean values (if available the “Innventia-method” was used) for all laboratories.
** Deviation from the combined mean values (+- %).

The In-house method for T_g differs mainly from Innventia-method by the heating rate (25 °C/min instead of 3 °C/min). The T_d was performed according to the Innventia-protocol.

13.1 Comments by lab 8

Three lignins (KLHM, KLSM and Organosolv) will be investigated.
The instruments used for all measurements were Netzsch STA 449F1 equipped with oven “Low Tempp Stell K”, Sensor/sample carrier DSC/TG Octo K.TA. The Innventia-methods for both T_g and T_d could not be used. No glass transition could be observed for lignin KLSM.

14 Appendix Lab 9

Lignin	Method	T_g (°C)	T_g (Standard Deviation)	CV (%)	T_g (°C) MV *	Dev. MV (%) **
KLHM	Innventia	112.7	1.2	1	114.6	-1.7
KLSM	Innventia	166.3	0.6	0.3	160.0	3.9
Org.solv	Innventia	123	1.0	0.8	126.3	-2.6
Soda	Innventia	-	-	-		-
ESEL	Innventia	-	-	-		-

* Combined mean values (if available the “Innventia-method” was preferred) for all laboratories. ** Deviation from the combined mean values (+- %).

No Td reported.

14.1 Comments by Lab 9

Tg values are mean of triplicates. No glass transition could be observed for lignin soda and ESEL.

15 References

Nordström Y, Norberg I, Sjöholm E, Drougge R (2012)
A new softening agent for melt spinning of softwood kraft lignin
J. Appl. Polym. Sci. In press on line DOI: 10.1002/APP 38795

16 Innventia Database information

Title

COST Action FP0901
Round Robins of lignin samples
Part 2: Thermal properties

Author

Elisabeth Sjöholm, Fredrik Aldaeus, Ylva Nordström and Anders Reimann

Abstract

The intention of this Round Robin test was to settle common methods for isolated lignins for determination of the most fundamental thermal characteristics; T_g and decomposition temperature (T_d). Five lignin samples were used; kraft lignin from birch/aspen wood and pine/spruce, respectively, organosolv spruce lignin, soda wheat straw lignin and enzymatic treated steam explosion poplar wood lignin. The samples thus represent different raw materials and types of processing of interest in today's research and development. The samples were analysed with respect to common impurities and fundamental properties.

Nine laboratories participated in part or in all thermal analysis. The T_d was analysed by six-seven laboratories using a distributed Innventia method. For the T_g determination Six of the laboratories used an Innventia method and three used their in-house methods.

For the determination of the T_d, good reproducibility between the laboratories was observed irrespective of lignin sample type and purity.

The determination of the glass transition temperature (T_g), was more difficult for lignin samples containing large amounts of non-lignin components such as high ash content and/or high carbohydrate content. Eventual residues from proteins did not appear to obstruct the T_g (or the T_d) analysis. Consequently the best agreement between the laboratories for the T_g determination were for the two kraft lignin samples and the lignin sample obtained from enzymatic hydrolysis of steam explosion lignin. A large scatter in the data was obtained for the organosolv and soda lignin samples, respectively. A common observation was that the scatter in the T_g values was considerably less when the common (Innventia) method was used as compared to when all results were included.

Only two laboratories compared their In-house methods with the distributed Innventia method. No systematic difference could be observed between the two methods, but since one of the series represents single measurements, no real conclusions can be drawn from this part of the Round Robin. Thus, the importance of a certain method on the obtained T_g value remains to be settled.

Keywords

Lignin, Thermal treatment, glass transition temperature, T_g, decomposition temperature, T_d, differential scanning calorimetry DSC, Thermal gravimetric analysis, TGA

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