This is the author version published as:

1   **Chemical and Thermal Properties of Bagasse Soda Lignin**
2   by
3   **P. Mousavioun and W.O.S. Doherty**

4   Centre for Tropical Crops and Biocommodities, Queensland University of
5   Technology, GPO Box 2343, Brisbane, Australia

6

7 Abstract

8   A major challenge of the 21st century will be to generate transportation fuels using

9   feedstocks such as lignocellulosic waste materials as a substitute for existing fossil

10   and nuclear fuels. The advantages of lignocellulosics as a feedstock material are that

11   they are abundant, sustainable and carbon-neutral. To improve the economics of

12   producing liquid transportation fuels from lignocellulosic biomass, the development

13   of value-added products from lignin, a major component of lignocellulosics, is

14   necessary. Lignins produced from black liquor through the fractionation of sugarcane

15   bagasse with soda and organic solvents have been characterised by physical and

16   chemical means. The soda lignin fractions have different physico-chemical properties

17   from each other, and have been compared to bagasse lignin extracted with aqueous

18   ethanol.

19 1   Introduction

20   In the last century, energy sources have been derived from petroleum (30 %), natural

21   gas (23 %), coal (22 %), renewable (19 %) and nuclear (6 %) (Song., 2002). In the

22   chemical industry, 4 % of crude oil and 31 % of natural gas are used in the

23   manufacture of platform chemicals and composite materials. The state of the oil

24   market ($US 40-$US100 per barrel) is unpredictable because of economic and

25   political pressures, and the ever increasing oil demand from developing Asian

26   countries will probably maintain the current high price of crude oil. There is the

27   ongoing debate among geologists as to the time frame when oil reserves will be

28   depleted. There is also the strong push towards reduced greenhouse gas (GHG)

29   emission. Fossil fuels used in transportation contribute over 25 % of GHG. It has

30   been estimated that the utilisation of plant/crop-based feedstock for the production of

31   chemicals in the European Union could deliver GHG reductions of over 6 M tonnes

32   per annum in the next decade. As a consequence of these events, there has been

33 coordinated R&D strategy across the globe for the utilisation of plant/crop-based
34 products.

35 The International Energy Agency, Energy Outlook in November 2006 said, "Rising
36 food demand, which competes with biofuels for existing arable and pasture land, will
37 constrain the potential for biofuels production using current technology". Such a
38 constraint causes feedstock price increases for both food and fuel. So the challenge
39 we now have is to be able to produce transportation fuels from non-food sources e.g.,
40 bagasse, wheat straw, rice stalk, cotton linters, agricultural wastes, and forest thinning,
41 at an economically competitive price without government subsidies. To bring down
42 production cost of biofuels, developing a market for lignin products which have
43 equivalent properties as the petroleum-based products is necessary.

44 In 2006, the world produced 1.4 billion tonnes of sugarcane (FAO, 2008). This
45 equates to ~400 million tonnes of bagasse. Currently, a vast majority of bagasse is
46 used to produce low value co-generation of power, manufacture of pulp and paper
47 products and furfural production. However, with continuing improvements in energy
48 efficiencies of sugar factories, more and more bagasse will be available for other
49 applications, such the production of cellulosic ethanol. The advantage bagasse has
50 over other non-food sources is that it is located centrally due to existing transportation
51 infrastructure. So, co-location of a cellulosic ethanol plant to a sugar factory gives the
52 opportunity to share production systems but also to share processing facilities.

53 Bagasse, an non-wood consist mainly of cellulose (50 %), hemicellulose (30%) and
54 lignin (20%). Lignin is an amorphous large, cross-linked, macromolecule with
55 molecular masses in the range 1000 g/mol to 20,000 g/mol. The degree of
56 polymerisation in nature is difficult to measure, since it is fragmented during
57 extraction and the molecule consists of various types of substructures which appear to
58 repeat in a haphazard manner. There are three monolignol monomers, methoxylated to
59 various degrees: p-coumaryl alcohol, coniferyl alcohol, and sinapyl. Despite
60 improvements in structure elucidation, the exact structure of lignin is still unknown.
61 The consensus by a number of workers (Adler, 1980; Sjostrom, 1981; Chen, 1991;
62 Ede and Kilpelaeinen, 1995; Karhunren et al., 1995a; Karhunen et al., 1995b) is that
63 the two commonest linkages is ether and carbon-carbon bonds. The phenylpropane β-
64 aryl ether linkages constitute the largest proportion of the different linkages

65 connecting the monomeric units. These linkages need to be broken for effective
66 lignin fractionation from biomass.

67 The processes used in the extraction of lignin from woody plants are conducted under
68 conditions were lignin is progressively broken down to lower molecular weight
69 fragments resulting to changes to its physico-chemical properties. Thus, apart from
70 the source of the lignin, the solvating ability of the solvent to either lignin or the
71 cellulose, or both, the properties of the solvent to inhibit to C-C bond formation, the
72 solution pH and the method of extraction influences the chemical and functional
73 group composition of lignin. Gosselink et al. (2004) have reported that lignin
74 composition is different not only among plants but also different between parts of the
75 same plant. The structural heterogeneity of lignin has also been studied by various
76 methods in a number of investigations. In several of these studies the lignin was
77 subjected to fractionation prior to the analysis (Robert et al., 1984; Moerck et al.,
78 1986; Vanderlann and Thring, 1998; Wallberg et al., 2003). These fractionations
79 were analysed for functional groups, elemental composition and molecular weight.
80 The results of these investigations showed that the fractionation process separated the
81 lignin into distinct molecular weights and that there were differences in the carboxylic
82 acids, phenolic hydroxyl and methoxyl contents The properties of the materials
83 produced were dependent on these structural properties

84 As our research goals are to produce cellulosic ethanol from bagasse via pretreatment
85 with soda and add value to soda lignin, we have undertaken a characterisation
86 exercise on soda lignin and examined its heterogeneity through sequential extraction
87 in order to target products based on structure-property relationships. Where possible
88 we have compared the results to that of bagasse lignin obtained through aqueous
89 ethanol extraction, as the lignin obtained by this process is generally regarded to be of
90 good quality.

2   Materials and methods

2.1   *Lignin extraction*

93 Bagasse was obtained from a Mackay Sugar Mill, Queensland Australia. It was wet
94 depithed and then air dried. Lignin was extracted from bagasse by the soda process
95 using a 20 L Parr reactor. In this method, 1 kg of bagasse is cooked with about 10.5 L

of 0.7 - 1 M NaOH. Once the reactor reaches the operating temperature of 170°C, it is maintained for 1.5 h. After cooling, the liquid (black liquor) was removed from the bottom of the reactor and sieved to remove fibrous material. To the black liquor, dilute sulphuric acid was slowly added with stirring to pH 5.5. Near pH 5.5 an obvious change in the appearance of the solution occurs; from black to murky brown. This change is due to the initial stages of lignin precipitation. The mixture was stirred for 10-15 min after which acidification is continued to pH 3. It was then transferred to a 65 °C water bath and stirred using an overhead stirrer for 30 – 45 min. The mixture was then vacuum filtered to recover the lignin. The lignin was repeatedly washed with hot water until all signs of foaming have subsided. It was then left to air-dry before being further dried in a vacuum oven at 45 °C overnight. This procedure increases the purity of lignin by reducing the inclusion of ash and carbohydrate components. It is different from other procedures reported in the literature because it is based on a two-stage acid precipitation process. The initial precipitation process at pH 5.5 produces lignin particles of high purity which are then allowed to grow to larger sizes before proceeding to the second precipitation stage where the proportion of impurities is highest.

Organosolvo lignin (OL) was obtained through precipitation of the black liquor into a dilute H_2SO_4 solution. The black liquor was obtained by the delignification of bagasse with 50 % aqueous ethanol solution in the 20 L Parr reactor. Crude lignin was dissolved in 0.1 M NaOH equilibrated and precipitated with H_2SO_4 at pH 3. The slurry was filtered hot and the residue was washed with water until the filtrate became colourless. The lignin was air dried and further dried at 45°C and 100°C, consecutively.

2.2   Lignin fractionation

Soda lignin is a complex and heterogeneous mixture with a rather broad molecular weight distribution. Sequential fractionation has been carried out to separate the lignin into three fractions of distinct molecular weight/size and chemical functionality. Ether and methanol are the solvents used in this study as was used by Thring et al. (1996) to fractionate ALCELL lignin.

To fractionate soda lignin, ~ 100 g and 250 mL diethyl ether are added to a large Schott bottle (1 L) or beaker (1 L). The container is covered and the contents are then

128   stirred for 20 min before being left to settle for 10 min. The diethyl ether is then

129   decanted off into another container. The remaining solid is then subjected to the same

130   treatment. This is repeated until the supernatant diethyl ether is a light yellow colour

131   when decanted off. The lignin residue is allowed to dry before this process is repeated

132   using methanol in place of ether. The diethyl ether fraction (L1) and methanol

133   fraction (L2) are either recovered using the rotary evaporator to evaporate off the

134   solvent, or acid is used to precipitate the lignin, followed by filtration to recover the

135   solid lignin. All 3 fractions of lignin (L1, L2 and the remaining residue, L3) are then

136   dried and weighed.

137   The OL was not fractionated in this study.

2.3 *Lignin characterisation methods*

2.3.1 Elemental analysis

140   Elemental analysis was performed on the three lignin fractions as well as the starting

141   lignin material using a FLASHEA 1112 Elemental Analyser instrument. In preparing

142   the samples for analysis, first they were dried at 100°C overnight, to remove any

143   moisture. To measure carbon, hydrogen and nitrogen contents, 2 to 4 mg samples

144   were encapsulated in a tin container, and for measuring oxygen content 2 to 4 mg

145   samples were encapsulated in a silver container. The analysis results were obtained

146   via gas chromatography, and compared with those of standard materials.

2.3.2 Ash analysis

148   Crucibles were pre-dried to constant weight in a muffle furnace at 575°C. Lignin

149   samples (0.5 g - 2 g) were weighed into the crucibles and heated to 105°C to remove

150   moisture. The crucibles were then heated at 575°C to constant weight. The weight of

151   ash remaining was calculated as a percentage of the original dry weight of sample

152   (Sluiter et al., 2008a).

2.3.3 Sugar analysis

154   Aliquots of 3 mL of 72 % H_2SO_4 were added to 0.3 g samples of lignin in pressure

155   tubes. The tubes were placed in a water bath at 30°C for 1 h and stirred intermittently

156   to completely wet the lignin sample. The acid was then diluted to 4 % through the

157 addition of water and the samples were autoclaved in pressure tubes at 121°C for 1 h

158 (Sluiter et al., 2008b). The samples were filtered with porcelain crucibles to remove

159 solids and the liquid fraction was analysed by HPLC for glucose, xylose and

160 arabinose.

2.3.4 Purity analysis

162 The purity of the lignin samples was calculated from the sum of ash and sugar results.

163 Due to the nature of the pulping and precipitation techniques, a significant amount of

164 ash and sugars may be present if the sample is not copiously washed with distilled

165 water.

2.3.5 Characterisation of functional groups

167 To predict the properties of lignin and its fractions, different functional group analyses

168 were performed. The functional groups quantified were the methoxyl group,

169 carboxylic acid functional group, phenolic hydroxyl group and total hydroxyl group

170 contents.

2.3.6 Methoxyl content method

172 The classical method for methoxyl determination of lignins uses hydroiodic acid to

173 promote demethylation and gas chromatography to determine the methoxy content

174 (Girardin et al., 1983). A less tedious method involves the use of proton NMR (Dos

175 Santos and Aberi, 1995). This was used in this project. Prior to NMR analysis, the

176 lignins were acetylated. The signals of syringyl protons are registered between 6.28

177 ppm and 7.00 ppm, while the signals of guaiacyl protons are registered between 7.00

178 ppm and 8.00 ppm (see Figure 1). The theoretical ratios between aromatic and

179 methoxyl protons of guaiacyl and syringyl are 1.00 ppm and 0.33 ppm respectively.

180 Measuring the ratios from the NMR spectra of acetylated lignins in deuterated

181 chloroform and submitting the data to a statistical linear regression analysis, the %

182 methoxyl (OCH_3) content can be obtained from the equation (1):

183

184 $\% \ OCH_3 = 28.28436 - 19.750047x$ 　　　　　　　　　　　　(1)

185 where; $x = H(aromatic)/H(methoxyl)$

2.3.7   Carboxylic acids and phenolic hydroxyl groups method

Carboxyl groups are believed to be present in native lignin, in extremely low concentrations. However, when native lignin is subjected to chemical or biological treatments, carboxyl groups are frequently detected in significant quantities. Therefore, quantitative measurements of carboxyl groups may provide information regarding the degree to which the lignin has been degraded or modified as a result of treatment.

A titration method was used in this work (Dence, 1992). The saturated KCl electrolyte generally used in calomel electrodes was replaced by a 1 M aqueous solution of tetra-n-butylammonium chloride (TnBACl). The titrant (0.05M TnBAH) was standardised through titration of benzoic acid in N,N' dimethylformamide (DMF) to a sharp inflection break.

The lignin sample and p-hydroxybenzoic acid were dissolved in a solution of distilled water, concentrated HCl and DMF. The solution was then titrated with 0.05 M TnBAH. There were three inflections in the titration curve. These correspond to: excess HCl and strong acids present in the sample, carboxylic acids, and phenolic hydroxyl groups, respectively.

A blank was also run on a solution of p-hydroxybenzoic acid, distilled water, HCl and DMF.

2.3.8   Total hydroxyl groups by acetylation method

The amount of total hydroxyl group in lignin was determined by potentiometry (Gosselink et al., 2004). The acetylation procedure given by Gosselink and co-workers (2004) is known to be unreliable because the acetylation of lignin is not complete. Therefore the procedure was slightly modified and the heating time extended from 1 h to 24 h. Approximately 0.5 g - 0.8 g of air-dried lignin was added to 10 mL of an acetic anhydride: pyridine (1:4 v/v) mixture. This was heated overnight in an oil bath at 90°C. After adding 2 mL water and 5 min stirring, 50 mL ethanol was added. Subsequently, the acetylated lignin was potentiometrically titrated with a standardised 0.1 M NaOH in ethanol.

2.3.9 Molecular weight determination

As lignin from different crops or treatments can be extremely diverse in structure, it is necessary to determine these differences through analytical methods. The molecular weight of a polymer can be a good indication of its strength as well as other physical properties. Size exclusion chromatography is a simple technique that can be utilized to determine the molecular weight of lignin.

Lignin samples were prepared in eluent (0.1M NaOH) at 0.2 mg.mL^{-1} just prior to analysis and filtered through a 0.45 µm syringe filter before running. Sodium polystyrene sulphonate standards of molecular weights 4,950 g.mol^{-1}, 16,600 g.mol^{-1}, 57,500 g.mol^{-1}, 127,000 g.mol^{-1}, 505,100 g.mol^{-1} and 1,188,400 g.mol^{-1} used to prepare a standard calibration curve. Lignin weight average molecular weight (M_w) and number average molecular weight (M_n) were calculated using the equation obtained from the trend line of the standard curve.

2.3.10 Particle size distribution

A Malvern Mastersizer was used to determine the particle size distribution of lignin. The lignin was dispersed in water and ultrasonicated before a laser beam was shown through the solution.

2.3.11 Thermogravimetric analysis (TGA)

Approximately 10 mg of sample was weighed into an aluminium pan and placed in the thermogravimetric analyser (TGA). Heating was at a rate of 10°C.min^{-1} and was performed from room temperature to approximately 800°C. The test was performed in an atmosphere of nitrogen, which was injected at a flow rate of 15 mL.min^{-1}. A curve of weight loss against temperature was constructed from the data obtained by the instrument. A derivative of this curve (dTG) was produced to indicate the temperatures at which maximum rates of weight loss occurred.

2.3.12 Differential scanning calorimetry (DSC)

Approximately 10 - 15 mg of lignin was precisely weighed and then encapsulated in an aluminium pan. The pan was then placed in a DSC-Q100 instrument and heated from 0°C to 200°C at a heating rate of 10°C.min^{-1} (cycle 1). The test was performed in an atmosphere of nitrogen, which was injected at a flow rate of 15 mL.min^{-1}.

246 Samples were then cooled down at a rate of 30°C.min^{-1}, to -10°C (cycle 2). Samples
247 were then reheated to 200°C at a rate of 10°C.min^{-1} (cycle 3). The plot obtained from
248 this second heating run shows the T_g as a step transition.

249 3 Results

250 *3.1 The fractionation process*

251 Only a very small portion of the original lignin sample, ~8%, was recovered using
252 diethyl ether (L1). The major proportion, ~ 68%, methanol soluble (L2), and the
253 residual lignin make up the remaining 24% (L3). Similar fractional yields (within 1
254 %) were obtained in repeat experiments, demonstrating the reproducibility of the
255 fractionation procedure. The results clearly show the heterogeneity of bagasse soda
256 lignin. For the OL, values of 24% for L1, 50% for L2 and 23% for L3 were obtained.
257 Thring et al. (1996) using a similar fractionation procedure obtained values of 27%
258 for L1, 53% for L2 and 18% for L3 for an ALCELL lignin extracted from mixed
259 hardwood. Based solely on the fractionation data, it appears that the organosolvo or
260 ALCELL lignin is more polydispersed than the soda lignin produced in this project.

261 *3.2 Elemental analysis results*

262 The elemental analysis results of the lignin and its three fractions are shown in Table
263 1 as well as bagasse OL lignin. The data show that carbon and hydrogen contents
264 decreases from L1 to L3. The hydrogen content is highest with L2. The nitrogen
265 contents of the soda lignin and its fractions are similar to that of OL, the value for OL
266 is slightly higher. The protein contents in the soda lignin are in the range 0.6% to
267 2.5% if a conversion factor of 6.26 is used. The protein content is low in soda lignin
268 because proteins are alkaline soluble and are easily removed during the lignin
269 recovery process.

270

271 **[Insert Table 1 here]**

272

273 Atomic ratios are calculated using values in Table 1, neglecting the nitrogen contents,
274 to give the empirical formulae of the different lignins (Table 2). In lignin chemistry

the empirical formula of the macromolecule is commonly given as a hypothetical hydroxyphenyl structural unit. This is known as the C_9-formula, with six carbon atoms in the benzene ring plus three carbon atoms making up the propyl side-chain. The results are shown in Table 2. Worth noting, though not surprising, is that the C_9 formula of L2 is similar to that of OL.

[Insert Table 2 here]

3.3   Sugar analysis results

The sugar and ash contents of lignin and its fractions are shown in Table 3. The purity of the original soda lignin, L1 and L2 are comparable to OL. The low purity of L3 is related to the high ash, xylan and glucan values. For all these samples lignin and xylan seem to be most strongly associated with the phenolic residie since xylan is present in each lignin type.

Energy dispersive spectroscopy indicated that the main element (>90%) in the ashed lignin samples is silicon. This is expected since sugarcane bagasse (from which the lignins were extracted) contains high silica content. Minor amounts of sodium, iron and potassium were also detected.

[Insert Table 3 here]

3.4   Molecular weight and functional groups

Table 4 shows M_n and M_w results of the soda lignins and OL. The molecular weight of the soda lignins increases from L1 to L3. For these lignins, their polydispersity are similar, with values around 1.1. This indicates that each fraction essentially contains lignin of the same chain length.

As shown in Table 4, the methoxyl content of the OL is higher than that of the soda lignins. This means that for bagasse, lignin is demethoxylated to a greater extent

303 during the soda extraction process (Thring et al., 1996) compared to the organosolvo

304 process.

305 The methoxyl group content of the soda lignin fractions increases with molecular

306 weight. This increase is not related to molecular weight but related to the insolubility

307 of syringal dominated lignin macromolecule in the ether and methanol solvents used

308 in the sequential fractionation process (Thring et al., 1996).

309

310 **[Insert Table 4 here]**

311

312 The hydroxyl and carboxylic acid contents were highest with the ether-soluble L1.

313 Soda pulping generally increases the carboxylic acid contents of lignins relative to

314 organosolv pulping (Gosselink et al., 2004).

315 *3.5   TGA results*

316 The results for the thermal decomposition of soda lignin, soda lignin fractions (i.e. L1,

317 L2 and L3), and OL are in Figures 2 – 5. The decomposition profiles of L2 and the

318 starting lignin material are similar. The TGA/dTG curves of all the samples

319 predominantly show a two-step (neglecting water loss) thermal decomposition

320 process, though L2, L3 and the original lignin material in addition, have shoulders at

321 higher temperatures. The two-stage decomposition process is more prominent the

322 thermograms for L1 and L3.

323 The first weight loss occurring at ~175°C is associated with water loss. The second

324 weight loss (i.e. the first decomposition stage) with a peak temperature of 300°C -

325 310°C is mainly associated with hemicellulose (i.e. xylan) decomposition. The second

326 stage (peak temperature > 330°C) is due to cellulose (i.e. glucan) and lignin

327 decomposition (Garcìa-Pèreza et al. 2001). The maximum decomposition

328 temperature of L1 is 380°C. For L2, L3 and the starting lignin material, although

329 75% decompose at temperatures lower than 380°C, the reminder 25% decompose at

330 temperatures > 400°C.

331 In summary, the TGA results clearly show that that lignin starts to degrade at around

332 200°C and so in the preparation of lignin-based blends, the working temperatures

333 should not exceed 200°C to 250°C.

334

[Insert Figure 2 here]

335

336

[Insert Figure 3 here]

337

338

[Insert Figure 4 here]

339

340

[Insert Figure 5 here]

341

342

3.6   Glass transition temperature

343

The DSC results for cycle 3 for the soda lignins, as well as OL, are shown in Figure 6. The results were processed using "Universal 4.2E TA" software. Table 5 shows the T_g of the lignins. It shows that the T_g of the soda lignins increased with increase in molecular weight.

344
345
346
347

348

[Insert Figure 6 here]

349

350

[Insert Table 5 here]

351

4   Discussion

352

The results of this work have confirmed the heterogeneity that exists in soda lignin. The lignin fractions obtained via sequential extraction were different in carboxylic acid, methoxy, phenol hydroxyl, ash and sugar contents, as well as on molecular weight. There is some similarity in the molecular weight averages between the soda fraction obtained with methanol i.e. L2 and the organosolvo lignin, OL.

353
354
355
356
357

The high purity of L1 and L2 suggests that they can be used in applications were organosolvo lignin have been used.

358
359

360   With the highest phenolic hydroxyl group, L1 has the highest potential to react with
361   oxyalkylating modification reagents such as ethylene oxide and propylene oxide.
362   This would improve the compatibility between lignin and polyolefins and improve the
363   dispersion of lignin in the polyolefin network. Also with its lowest methoxy content,
364   it possesses additional sites that can aid the ease of lignin functionalisation.

365   The high phenolic nature of the starting material and L1 (and to a lesser extent L2)
366   translates into good reactivity with formaldehyde in phenol formaldehyde and epoxy
367   resins. L3, though with a high ash content, will also be suitable for making phenol
368   formaldehyde resins because of its high sugar content (glucan and xylan).

369   The high phenolic and carboxylic acid groups in L1 and L2 translate to an increase in
370   elastic character through hydrogen-bond structuring necessary for making paints.

371   For lignin to be used in free radical polymerisation reactions for the syntheses of
372   resins and paints, its solubility can be improved in monomers such as styrene and
373   methyl methacryalate by reacting the hydroxyl groups with acid anhydrides.
374   Fractions L1 and L2 which are high in phenolic hydroxyl groups will readily react to
375   form the desired ester, and because of the presence of high carboxylic acid content
376   there is greater probability of increase in elastic character of the product through
377   hydrogen-bond structuring.

378

References

380   Dence, C. W. 1992. Determination of carboxylic groups. In Methods in lignin
381   chemistry Lin, S. Y., Dence,C.W., Ed. Springer: Berlin, pp 458-464.

382

383   Dos Santos Aberu, H. a. F., M., 1995. An. Bras.Ci. 379.

384

385   Ede, R.M., Kilpelainen, I., 1995. Homo- and Hetero-Nuclear 2d nMr Techniques:
386   Umambiguous Structural Probes for Non-Cyclic Benzyl Aryl Ethers in Soluble Lignin
387   Samples. Res. Chem. Intermed. 21, 313-329

388

389 Garcìa-Pèreza, M., Chaala, A., Yanga, J., Roy, C. 2001. Co-pyrolysis of sugarcane
390 bagasse with petroleum residue. Part I: thermogravimetric analysis. Fuel, 80.

391

392 Girardin, M.; Metche, M. 1983. Microdosage rapide des groupements alkoxyles par
393 chromatographie en phase gazeuse: Application à la lignine. Journal of
394 Chromatography A, 264, 155-158.

395

396 Gosselink, R. J. A.; Abächerli, A.; Semke, H.; Malherbe, R.; Käuper, P.; Nadif, A.;
397 van Dam, J. E. G. 2004. Analytical protocols for characterisation of sulphur-free
398 lignin. Industrial Crops and Products, 19, (3), 271-281.

399

400 Moerck, R.; Yoshida, H.; Kringstand, K. P.; Hatakeyama, H., Fractionation of kraft
401 lignin by successive extraction with organic solvents, 1. Functional groups, 13C-
402 NMR-spectra and molecular weight distributions. Holzforschung 1986, 40, 51-60.

403

404 OECD-FAO Agricultural outlook 2008-2017. www.agri-outlook.org

405

406 Robert, D. R.; Bardet, M.; Gellerstedt, G. r.; Lindfors, E. L., Structural Changes in
407 Lignin During Kraft Cooking Part 3. On the Structure of Dissolved Lignins. Journal
408 of Wood Chemistry and Technology 1984, 4, (3), 239-263.

409

410 Sluiter, A. H., B. Ruiz,R. Scarlata,C. Sluiter,J. and D. Templeton Determination of
411 ash in biomass:Laboratory Analytical Procedure (LAP); NREL Report No. TP-510-
412 42622; 25.4.2008, 2008.

413

414 Sluiter, A. H., B. Ruiz,R. Scarlata,C. Sluiter,J. Templeton,D. and Crocker,D.
415 Determination of Structural Carbohydrates and Lignin in Biomass Laboratory
416 Analytical Procedure (LAP); NREL Report No. TP-510-42618; 2008.

417

418   Song, C., 2002. Fuel processing for low-temperature and high-temperature fuel cells -

419   Challenges, and opportunities for sustainable development in the 21st century Catal.

420   Today 77, 17-49.

421

422   Thring, R. W. V., M. N.; Griffin, S. L., Fractionation of ALCELL lignin by sequential

423   solvent extraction. Wood Chemistry and Technology 1996, 16, (2), 139-154.

424

425   Vanderlaan, M. N.; Thring, R. W., Polyurethanes from Alcell® lignin fractions

426   obtained by sequential solvent extraction. Biomass and Bioenergy 1998, 14, (5-6),

427   525-531.

428

429   Wallberg, O.; Jönsson, A.-S.; Wimmerstedt, R., Fractionation and concentration of

430   kraft black liquor lignin with ultrafiltration. Desalination 2003, 154, (2), 187-199.

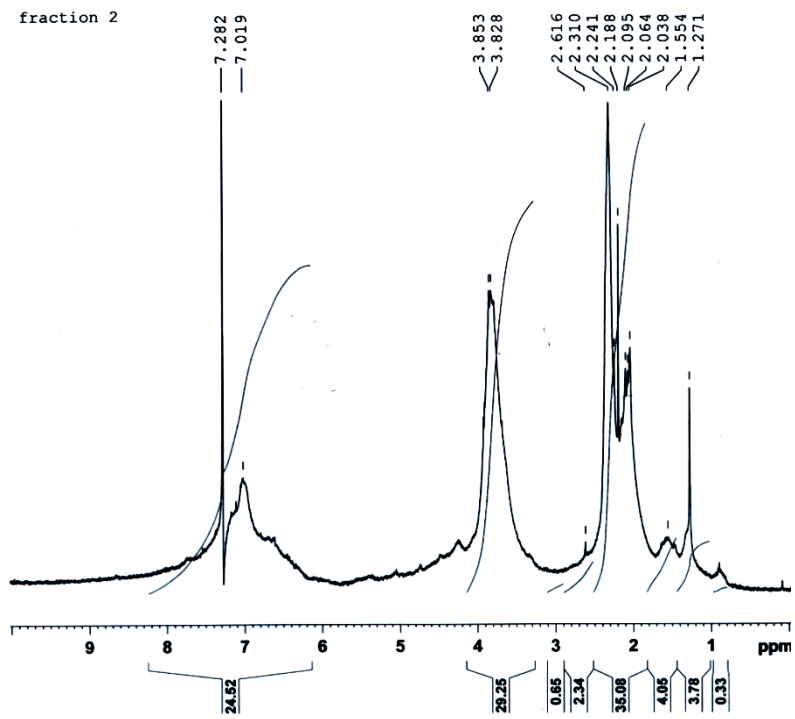# Attachments of Chemical and Thermal Properties of Bagasse Soda Lignin

Figure 1   NMR spectrum of an acetylated lignin fraction (L2)

Table 1   Elemental analysis of lignins (wt%)

Sample	N	C	H	O
Starting lignin	0.4	63.7	5.7	22.9
L1	0.1	77.7	7.0	18.2
L2	0.3	59.8	5.7	26.8
L3	0.3	47.1	4.9	25.7
OL	0.5	62.1	6.2	29.0

Table 2   Lignin formulae

Sample	Empirical formula	C_9 formula
Starting lignin	$C_{5.31}H_{5.66}O_{1.43}$	$C_9H_{9.59}O_{2.42}$
L1	$C_{6.47}H_{6.94}O_{1.14}$	$C_9H_{9.65}O_{1.59}$
L2	$C_{4.95}H_{5.65}O_{1.67}$	$C_9H_{10.27}O_{3.04}$
L3	$C_{3.92}H_{4.86}O_{1.60}$	$C_9H_{11.16}O_{3.67}$
OL	$C_{5.18}H_{6.18}O_{1.78}$	$C_9H_{10.73}O_{3.15}$

Table 3   Purity of lignins

Sample	Ash (% wt)	Glucan (% wt)	Xylan (% wt)	Arabinan (% wt)	Purity (% wt)
Starting lignin	2.0	0.2	1.6	<0.1	96.3
L1	0.2	0.0	0.2	<0.1	99.6
L2	1.0	0.1	0.5	<0.1	98.4
L3	9.5	3.9	10.0	0.37	67.0
OL	0.4	1.4	0.6	<0.1	97.6

Table 4   Molecular weight averages and function groups

Sample	M_n (g.mol^{-1})	M_w (g.mol^{-1})	Methoxy (%)	Phenolic OH (meq.g^{-1})	RCOOH (meq.g^{-1})	Total OH (meq.g^{-1})
Starting lignin	2410	2160	10.9	3	3.1	8.5
L1	500	560	3.1	2.5	7.7	16.1
L2	2 380	2 670	11.7	0.9	4.8	9.0
L3	5 350	5 990	12.5	0.2	1.4	4.3
OL	2 000	2 300	15.1			
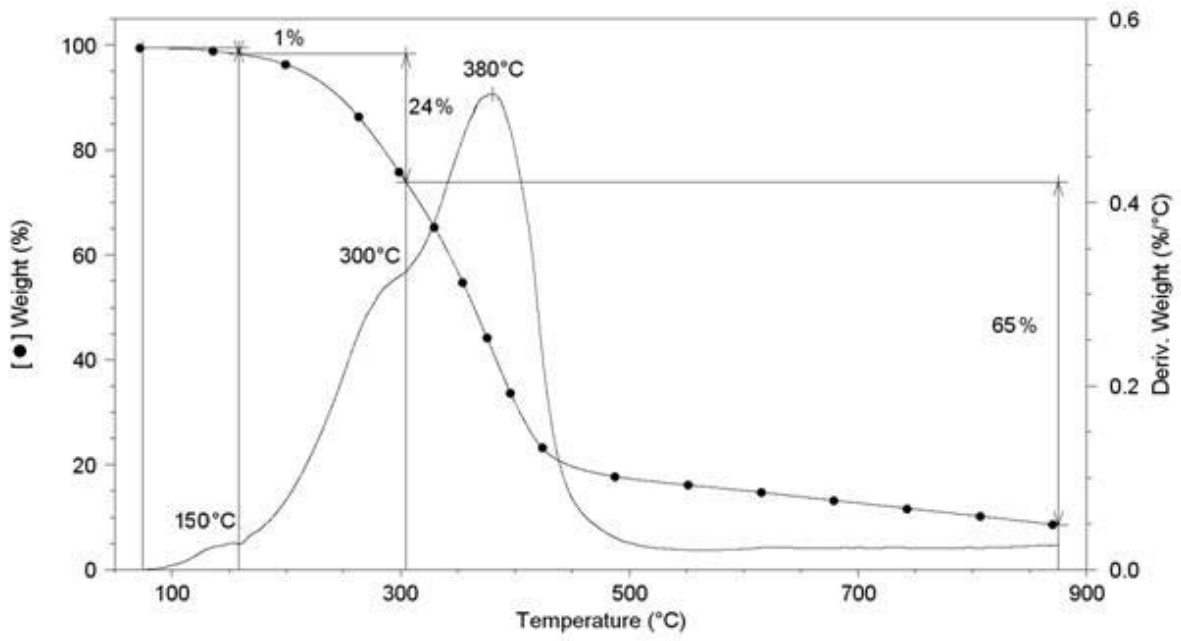
Figure 2   TGA/dTG curve of L1 performed under nitrogen atmosphere
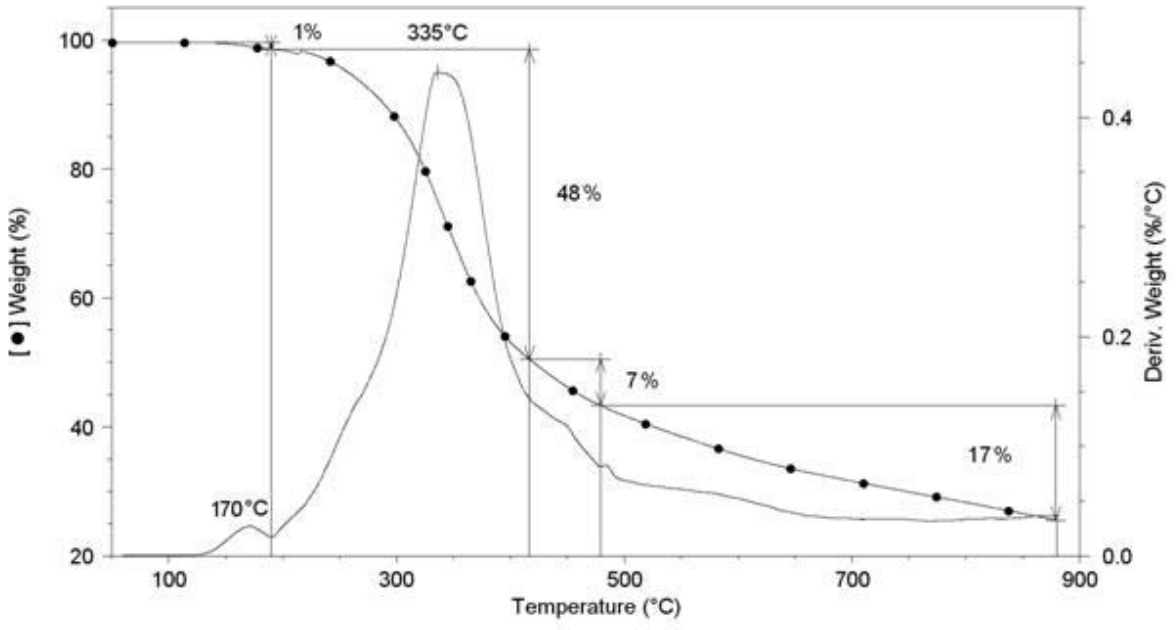
Figure 3   TGA/dTG curve of L2 performed under nitrogen atmosphere
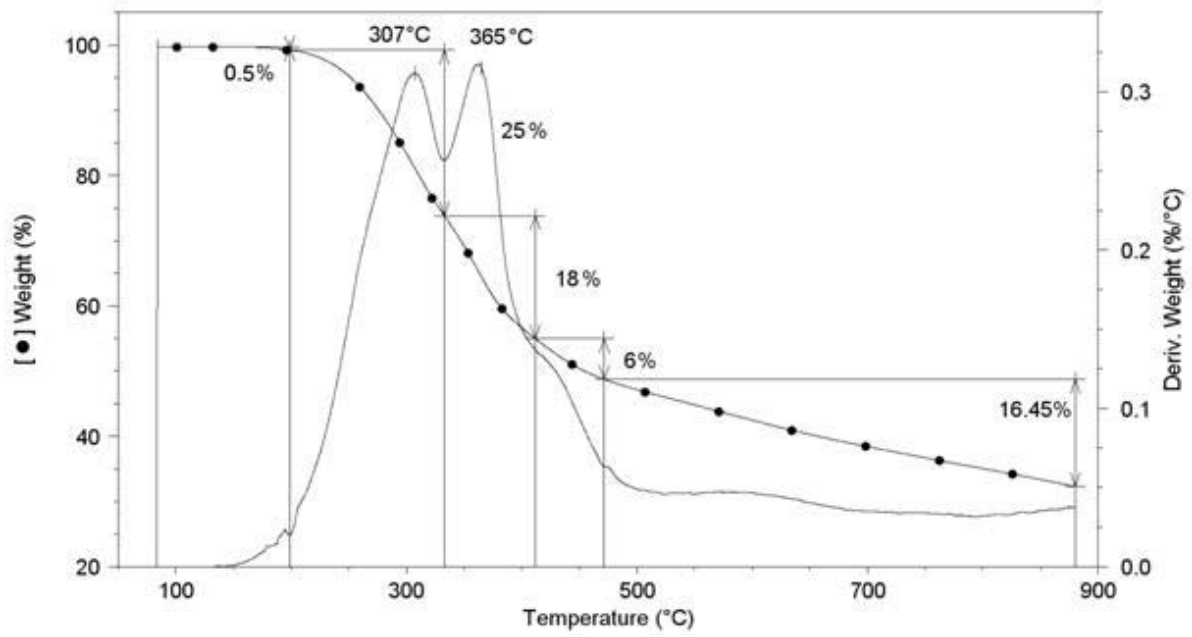
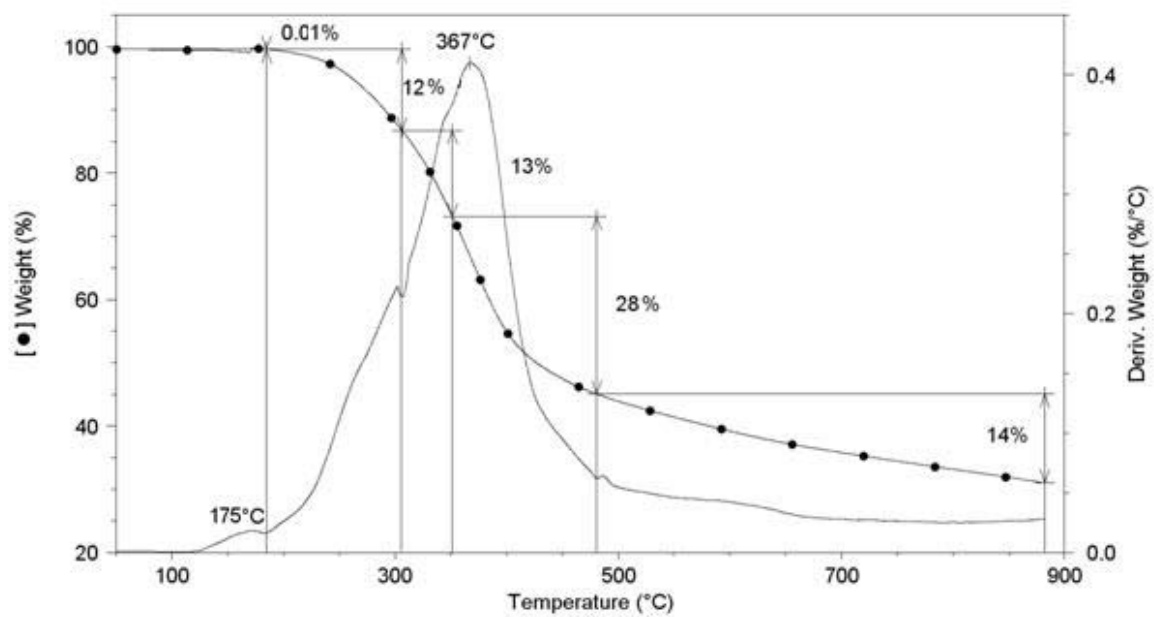Figure 4   TGA/dTG curve of L3 performed under nitrogen atmosphere

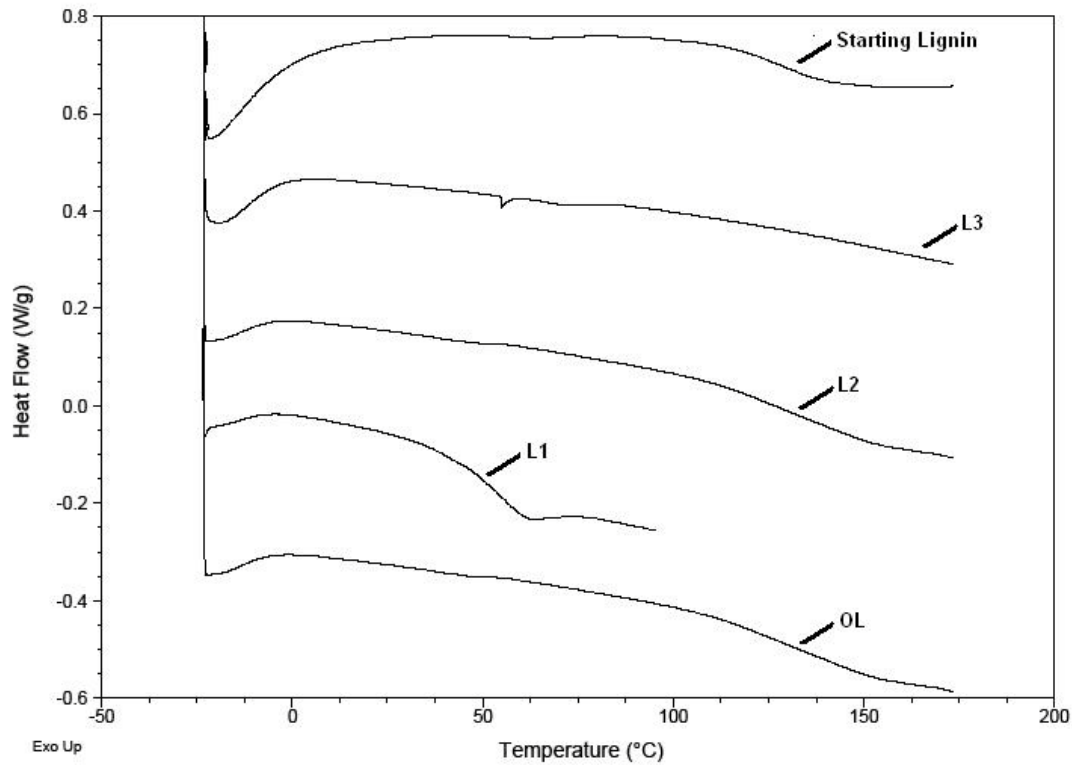Figure 5   TGA/dTG curve of the starting soda lignin performed under nitrogen atmosphere

Figure 6   DSC curves for lignin and its fractions

Table 5 T_g of lignin and fractions

Sample	T_g (°C)
Starting lignin	130
L1	51
L2	130
L3	154
OL	130