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Lignin–carbohydrate complexes from sugarcane bagasse: Preparation, purification, and characterization

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Abstract

Lignin–carbohydrate complexes were isolated from sugarcane bagasse by a process, which yielded sulfur-free lignins. These could be made carbohydrate-free, if necessary, by treatment with xylanase enzyme. A study of the preparation, purification, and characterization of such lignin–carbohydrate complexes, comparison with commercial lignin samples (wood based as well as bagasse based) and some other lignin derivatives was made by using a variety of analytical tools such as FTIR, HPLC at three different UV-wavelengths, GPC, thermal analysis and elemental analysis. The use of such a diverse range of lignin–carbohydrate complex samples enabled us to predict the sensitivity of the various analytical techniques for characterization of complex polymers containing carbohydrate moieties. Evidence for lignin–carbohydrate complex was detectable by FTIR as well as HPLC studies. Thermal analysis studies showed the crucial effect of carbohydrate groups, the content of aliphatic chains, and the sulfur content of the lignins. Generalized structures of lignin–carbohydrate complexes obtained from various sources using different preparation methods and chemical modifications are presented. This will aid the applications development effort with advantageously using lignins containing low levels of carbohydrate moieties as reactive sites as well as biodegradability inducing sites.

Keywords: Lignin–carbohydrate complex; Sugarcane bagasse; Xylanase enzyme; Biodegradability; Sulfur-free lignins; Hardwood lignins; Softwood lignins

1. Introduction

'Lignin is a multifunctional natural polymer that has the potential to be developed into a major industrial raw material for a multitude of applications (Chem. & Eng. News, 1980; Glasser, Barnett, Rials & Saraf, 1984; Glasser & Leitheiser, 1984; Goheen & Henderson, 1978; Goheen & Hoyt, 1981; Hatakeyama et al., 1989, chap. 15; Saraf & Glasser, 1984; Wu & Glasser, 1984). After cellulose and hemicellulose, lignin is considered to be the most abundant natural polymer present on planet earth. It is estimated that currently planet earth contains 300 billion metric tons of lignin, with an annual biosynthetic rate of production of 20 billion metric tons (Argyropolous & Menachem, 1998). Thus, with a perceived shortage of petroleum-based materials as well as a desire to utilize 'green materials', the chemistry and technology of lignins is seeing renewed interest.

The chemical structure, molecular weights, molecular weight distribution and degree of crosslinking of lignins depend upon the age of the plant from which it is isolated, the type of plant (hard wood, softwood, grasses, etc.). The purity of the isolated lignins depends upon the method of isolation (chemical/biochemical/mechanical), the purification strategy followed, and so on. In order to develop sophisticated applications of lignins, it is the most essential to have highly pure and well-characterized lignin samples. Detailed characterization studies of lignins have been reported in several papers over a period of several decades (Glasser et al., 1983; Lin & Dence, 1992, chap. 4–9; Sarkanen & Ludwig, 1971, chap. 5–8; Schuerch, 1952). Yet, the complexity of the structure, the variety of new innovative methods of isolation and purification, and improved instrumentation, leads to new assignments and interpretations of structural features of lignins (Fredheim et al., 2002; Gosselink et al., 2004; Majcherczyk & Hiittermann, 1997; Martinez et al., 1999; Rohella et al., 1996; Shevchenko & Bailey, 1996; Sun et al., 2003;

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Tsujiyama & Miyamori, 2000; Tucker et al., 2001; Varma, 1984, 1986; Xias et al., 2001), and forms the basis of ever-new research and development efforts.

In particular, lignins are rarely isolated as pure materials, and are always associated with carbohydrate linkages (cellulose, hemicellulose) to varying extents, depending on their isolation procedure. This small carbohydrate content (generally 2–8% by weight in commercial lignins) plays a crucial part in the final reactivity and properties of the polymer. Therefore, in this study, we have carried out a detailed characterization of our laboratory prepared lignin–carbohydrate complexes vis a vis commercial wood lignin, semi-commercial organosolv sugarcane bagasse lignin, xylan-free and sulfur-free lignin from bagasse, commercial lignosulfonate from softwood lignin, laboratory prepared liqnosulfonate from sulfur-free bagasse lignins, bagasse lignin–succinic acid adduct, and bagasse lignin succinate–crown ether adduct. Thus in all 12 samples of lignins, lignin–carbohydrate complexes, and other lignin derivatives (three commercial and nine prepared in our laboratory) were investigated and the results are elaborated in this paper. The techniques used for characterization are FTIR, HPLC, thermal analysis, elemental analysis, atomic absorption spectroscopy, and treatment with xylanase enzyme. These diverse lignin samples and diverse experimental techniques have given us a deeper insight into the structures, properties, and the limitations of detection of various features of lignins as a complex molecule. Effects of residual carbohydrate content in lignins, increasing aliphatic chain length, increased crosslinking, effects of small amount of sulfur content, etc. are shown in the changed spectral characteristics and will be valuable in evaluating lignins for new applications research. Our previous work (Galgali et al., 2002) has shown that functionalized polystyrenes, as model systems for lignins, can be made biodegradable by attaching as low as 1% by weight of carbohydrate moieties.

2. Experimental

2.1. General procedure for preparation of lignin–carbohydrate complexes

Indian sugarcane bagasse was crushed to a fine powder passing through a 100-mesh screen. It was subject to steam pressure ranging from 2 to 20 bar for a residence times of 2–15 min, followed by alkali digestion and bleaching sequences. This process yielded lignins containing 3–5% carbohydrate groups; these could be removed by treatment with a particular strain of xylanase enzyme developed in our laboratory. The details of the process are being patented.

2.2. Materials

The following lignin–carbohydrate complexes, carbohydrate-free lignins, and lignin derivatives were either prepared in our laboratory, or procured from alternate sources, as detailed below:

1. Indulin AT (Westvaco, USA) (LS1) is a commercially available wood based lignin–carbohydrate complex. A research sample was kindly provided to us by the company for our research work.
2. Sulfur-free ethanol/water organosolv bagasse lignin–carbohydrate complex (LS2) was prepared in a semi-commercial pilot plant of M/s Pudumjee Pulp and Paper Mills, Pune, and a sample was kindly provided to us by the company for our research work.
3. Sulfur-free and carbohydrate-free ethanol/water organosolv bagasse lignin (LS3) was prepared by treating (LS2) with xylanase by a proprietary process in our laboratory.
4. Sulfur-free bagasse lignin (LS4) was prepared in our laboratory by a proprietary steam-cum-alkali process followed by precipitation in HCl.
5. Sulfur-free carbohydrate-free bagasse lignin (LS5) was prepared in our laboratory by treating LS4 with xylanase by a proprietary process.
6. Low sulfur bagasse lignin (LS6) was prepared in our laboratory by a proprietary steam-cum-alkali process followed by precipitation in H_2SO_4.
7. Low sulfur carbohydrate-free bagasse lignin (LS7) was prepared in our laboratory by treating LS6 with xylanase by a proprietary process.
8. Wood based sodium lignosulfonate (LS8) was obtained commercially from M/s Chembond, Mumbai.
9. Bagasse based sodium lignosulfonate (LS9) was synthesized in our laboratory by a proprietary process using LS4 as a starting material.
10. Bagasse based sodium lignosulfonate (LS10) was synthesized in our laboratory by a proprietary process using LS6 as a starting material.
11. Bagasse lignin–succinic acid adduct (LS11) was prepared by the reaction of LS2 with succinic acid
12. Bagasse lignin–succinic acid–crown ether adduct (LS12) was prepared by the reaction of LS11 with *trans*-diaminodibenzo-18-crown ether.

3. Characterization

3.1. FTIR

A Perkin Elmer Spectrum 1 FTIR was used. The samples were used in the form of KBR discs, which were prepared by grinding 1 mg sample/100 mg pre-dried KBR. The spectra were recorded in the range of 450–4000 cm^{-1}.

3.2. HPLC

The lignins were subjected to liquid chromatography in order to compare their compositions. A Dionex HPLC

equipped with quaternary gradient pump, injector, multi-wavelength programmable UV detector was used for this purpose. The instrument set-up consisted of Aminex-HPX-87H column, an ion exclusion column with mobile phase consisting of 2.75 ml 10% H_2SO_4 in 1000 ml double distilled water.

Lignin samples were dissolved in 20 mM of NaOH and diluted with 1 mL of the mobile phase, filtered and 20 μL was injected to the column, the detection was carried out at three different wavelength 210, 254 and 272 nm.

3.3. Thermogravimetric analysis (TG)

The thermal stability of lignins was studied using Perkin Elmer TGA-7. The TG of various lignins and their derivatives were run up to 700 °C with a heating rate of 10 °C/min in nitrogen atmosphere.

3.4. Elemental analysis

C, H, N and S were estimated using Carlo Erba CHNS analyzer.

3.5. Atomic absorption spectroscopy

Determination of the Na content was performed using a Chemito Atomic Absorption Spectrophotometer, Model No. 201.

As is evident from Table 1, the C and H percentage are in close agreement for LS2, LS4 and LS6. Small percentage of nitrogen also appears for LS6, this could be due to the protein present in bagasse. Soda lignin contains considerable amounts of protein (Gosselink et al., 2004), this is evidenced by presence of nitrogen in the elemental analysis. Pan and Sano (2000) also found the presence of proteins in alkaline lignins of wheat straw. LS8, LS9 and LS10 show less carbon and hydrogen content due to sulfonation. The carbon and hydrogen content in LS11 and LS12 found to be changed could be due to the reaction of lignin and succunic acid in LS11 and further with crown ether in LS12. The presence of sulfur was due to sulfuric acid used in the precipitation of LS6 lignin.

Table 1
Elemental analysis

Lignin	%C	%H	%N	%S	%Na by AAS
LS1	59.57	6.29	1.07	2.16	1.042
LS2	62.84	5.37	–	–	0.074
LS3	62.17	5.49	–	–	–
LS4	62.95	5.74	–	–	0.049
LS5	61.87	6.25	0.96	–	–
LS6	62.18	5.72	0.43	1.11	0.416
LS7	61.44	6.34	0.97	–	–
LS8	45.75	4.49	–	4.94	–
LS9	44.25	4.54	–	4.20	8.75
LS10	44.25	4.54	–	4.20	–
LS11	58.47	4.81	–	–	–
LS12	60.71	5.16	1.54	–	–

3.6. Assignment of IR absorption of lignins

The various bands in the FTIR spectra of different lignin–carbohydrate samples were compared by calculating their ratio with the band obtained at 1510–1520 cm^{-1}, as shown in Table 2.

Fig. 1 shows FTIR spectra of LS1, LS4 and LS6 (i.e. lignin–carbohydrate complexes of softwood and bagasse). The differences between softwood and hardwood lignins have been published by Martinez (Martinez et al., 1999), and are in agreement with the above results. Thus, our FTIR studies confirm that Indian sugarcane bagasse lignin isolated by us, and being one of the largest known reservoirs of annually renewable resource (estimated at 200 million tonnes per annum), contains both syringyl and guaiacyl units, similar to hardwood lignins.

LS1 and LS6 contain about 2 and 1% sulfur, respectively. This is indicated by the C–S stretching at 619 cm^{-1} (virtually absent in LS2 and LS4) (Fig. 1). The IR spectra of both the LS4 and LS6 lignin are more or less similar in absorption peaks as well as in absorption intensities, except for the minor sulfur content in sulfuric acid precipitated LS6. Therefore, precipitation by HCl is a preferred method for isolating lignins. LS4 and LS6 lignin samples were treated with xylanase enzyme giving samples LS5 and LS7, respectively.

Fig. 2 shows the band at 1693–1705 cm^{-1}, indicative of C=O stretching, (due to carbohydrates linked with lignin), has drastically reduced after xylanase treatment (LS5). This is confirmed by significant reduction in the hydroxyl peak of LS5. Further evidence of this is seen by the reduction in relative absorbance at 1118 and 1269 cm^{-1} which is an indicative of C=O stretching present in carbohydrates (Lin & Dence, 1992). Similar trends have been observed in case of LS6 and LS7 after the xylanase treatment. The removals of carbohydrate linkage have also been observed in HPLC analysis.

Fig. 3 shows the FTIR spectra of lignosulfonates LS8 (softwood based), and LS9 and LS10 (bagasse based). A peak at 1710 cm^{-1} in LS8 (commercial lignosulfonate) could be due to the C=O stretching due to the carbohydrate linkage with lignin. This band is absent in lignosulfonates LS9 and LS10. It appears that carbohydrate groups in LS9 and LS10 prepared by other processes in the laboratory are hydrolyzed under the reaction condition of their preparation (basic aqueous medium, high temperature).

The band at 655 cm^{-1}, characteristic of lignosulfonate (Nada et al., 1998), appears at 650 cm^{-1} for LS8, and at 618–650 cm^{-1} for LS9 and LS10. The presence of sulfur has been confirmed by elemental analysis. This shows that the structure of lignosufonates prepared by the classical sulfite process (LS8) or by sulphonation of isolated lignins (LS9, LS10) are similar, therefore, there is good scope to

Table 2
FTIR studies: relative absorbance of various groups (absorbance of band/absorbance of aromatic ring maximum absorption)

Group	Band	LS1	LS2	LS3	LS4	LS5	LS6	LS7	LS8	LS9	LS10	LS11	LS12
O–H stretch	3400–3430	0.62	0.74	0.50	0.65	0.58	0.69	0.63	1.08	1.05	1.13	0.61	–
Aliphatic C–H stretch in CH_3 not in OCH_3; Phenolic OH	1360–1380	0.43	0.62	0.47	0.51	0.60	0.49	0.55					
S ring + G ring condensed (G ring substituted at position 5) C–C, C–O, C=O stretch; G condensed > G etherfied; 2 ndry OH aromatic C–H inplane deformation; typical for G units; primary OH	1328	–	0.60	0.60	0.64	0.65	0.62	0.63	–	–		1.28	0.54
	1218	0.76	0.92	0.86	1.01	0.81	0.99	0.83	1.3	1.23	0.93	2.10	0.6
	1170–1140	0.71	0.72	0.72	0.59	0.60	0.55	0.59	–	–		1.45	0.73
Aromatic C–H inplane deformation; G > S; C–O deformation in primary alcohols	1030–1045	0.67	0.34	0.46	0.47	0.58	0.46	0.54	1.38	1.09	0.86	0.17	0.95
Etheric O	1127	0.71	–	–	–	–	–	–				1.00	0.95
Aromatic C–H inplane deformation; typical for S units; secondary alcohols; C=O stretch (unconj.)	1118	–	0.82	0.8	0.96	0.85	0.93	0.86	–	1.15	0.93	–	–
CH stretch methyl and methylene groups	2934	0.42	0.40	0.40	0.47	0.51	0.44	0.54	0.72	0.82	0.80	0.72	0.38
C–H deformation	1462	0.76	0.74	0.76	0.8	0.82	0.79	0.81	0.77	1.0	0.93	0.83	0.73
Aromatic skeletal vibrations combined with C–H inplane deformation	1425	0.71	0.56	0.64	0.63	0.68	0.62	0.68	0.72	0.9	0.87	1.45	0.57
Vibration of aromatic skeletal; C=O stretch; S > G, G condensed > G etherified	1600	0.48	0.94	0.84	0.71	0.73	0.70	0.72	0.78	1.03	1.00	1.06	0.78
Aromatic skeletal vibrations G > S	1513	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
C–H out of plane at positions 2 and 6 of S units	835	–	0.16	0.16	0.34	0.39	0.33	0.27	0.19	0.47	0.27	0.01	0.54
C–H out of plane at position 2, 5 and 6 in G units	856	–	–	–	–	–	–	–	0.19	–	–	–	–
C=O stretch; *p*-aryl ketones, amides	1643	–	–	–	–	0.55	–	0.65	–	–	–	–	0.49
C=O in unconj. ketones, ester groups frequently from carbohydrates, conj. aldehydes, carboxylic acids	1696–1705	1.0	0.64	0.6	0.44	–	0.41	–	0.3	–	–	2.4	0.5
G ring: C=O stretch	1260–1269	1.0	0.84	0.81	0.8	0.67	0.77	0.73	–	–	–	1.22	0.89
C–S vibration of sulfonic group	651	–	–	–	–	–	–	–	0.5	0.54	0.4	–	–
C–S broad band	615	0.047	–	–	–	–	0.01	–	–	–	–	–	–

S, syringyl; G, guaiacyl.

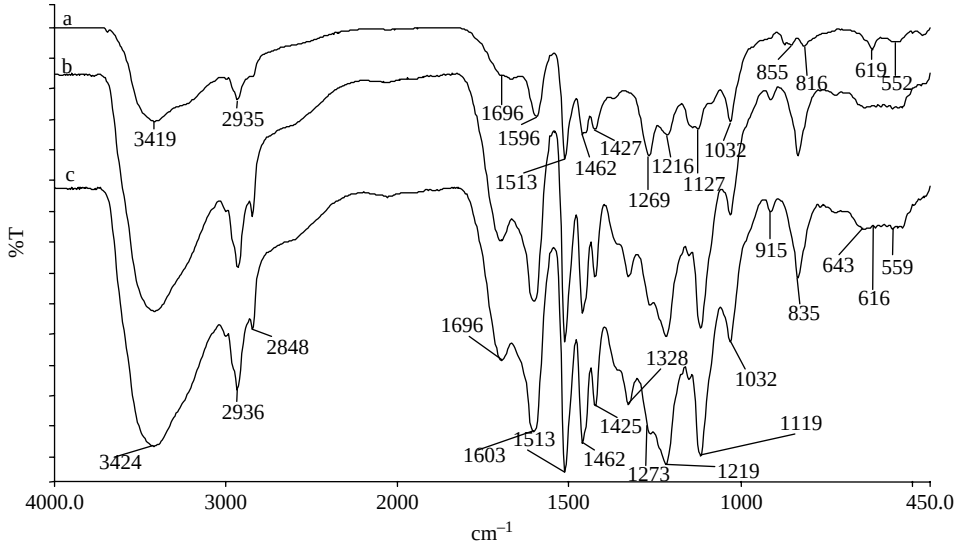

Fig. 1. FTIR of (a) softwood lignin–carbohydrate complex LS1, (b) bagasse lignin–carbohydrate complex LS4, and (c) bagasse lignin–carbohydrate complex LS6.

synthesize lignosulfonates from vast amount of waste lignins.

Fig. 4 shows the FTIR of lignin–carbohydrate complex (LS2) and its succinic acid and crown ether derivative (LS11, LS12). An amide bond is formed in LS12 (peak at 1654 cm^{-1}). The large amount of carbohydrates in LS2 is seen by the large peak at 3423 cm^{-1}, and it is decreased in LS11 and LS12. In the latter, the N–H stretch band merges with this hydroxyl peak. The ester peak in LS11 is clearly seen at 1708 cm^{-1}. However, crosslinking of succinic acid (LS11) by diamino dibenzo 18-crown-6 (LS12) reduces the resolution of the spectra, this is analogous to the lower resolution of poly(styrene–divinylbenzene) spectrum as compared to polystyrene spectrum (Fig. 5).

Thus, lignins isolated by various methods can be derivatised to interesting new compounds like LS11 and LS12 with vastly different thermal properties (see Section 3.7) and characterized by FTIR.

3.7. Thermal analysis

TG curves of various bagasse lignin–carbohydrate complexes as well as carbohydrate-free lignins were obtained under pure nitrogen atmosphere. Table 3 gives the TGA experimental details such as degradation onset temperature (T_{onset}) and maximum degradation temperature (T_{max}) for the thermal degradation of the various lignin samples and degradation wt% from analysis of TGA curves. The thermal curves show first stage of degradation at 100–150 °C due to the evaporation of residual moisture. The second degradation occurs at 230–300 °C is due to the carbohydrate (hemicellulose) component present in lignin.

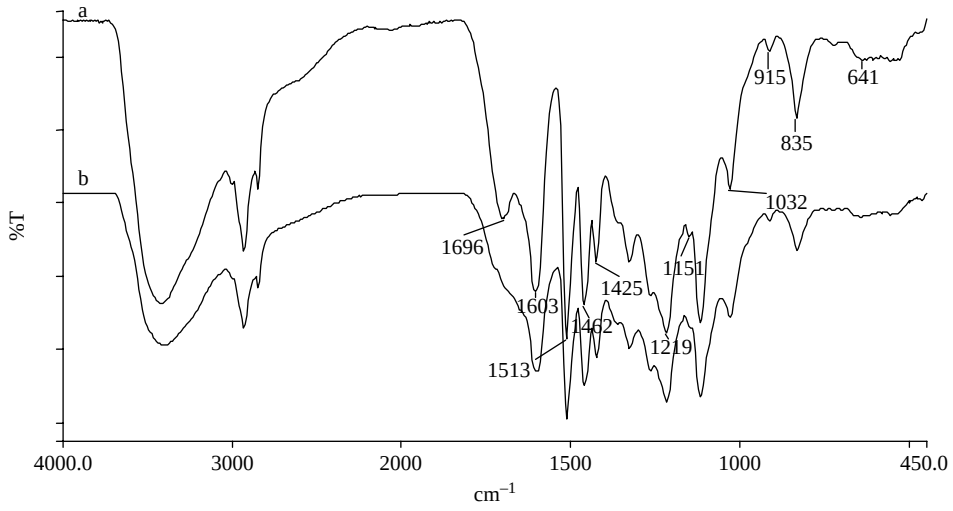

Fig. 2. FTIR of (a) bagasse lignin–carbohydrate complex LS4, and (b) carbohydrate–free bagasse lignin LS5.

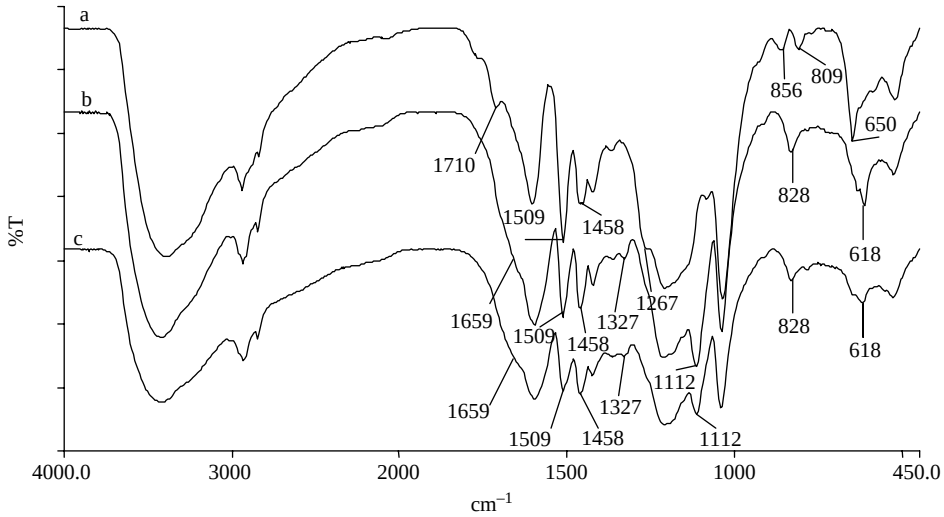

Fig. 3. FTIR of (a) commercial softwood lignosulfonate LS8, (b) bagasse lignosulfonate LS9, and (c) bagasse lignosulfonate LS10.

This, therefore, represents the upper limits of temperature for processing lignin–carbohydrate complexes. Lignin itself degrades above 300 °C and shows maximum degradation at 330–400 °C. In nitrogen atmosphere 40–50% residue was observed up to ∼600 °C. No residue is seen for polystyrene and crosslinked polystyrene. Apparently, the many functional groups present in lignins and their derivatives lead to complex crosslinked structures that do not decompose upto 600 °C.

Softwood based LS1, based on guaiacyl units, probably has more crosslinking sites and appears to get increasingly crosslinked and thermally stable as compared to LS4 and LS6. The THF soluble fraction (LS1A) of softwood based lignin (LS1) shows less thermal stability than the THF insoluble fraction (LS1B), which is apparently the fraction, which has very high crosslink density (Fig. 6).

LS2, LS4, and LS6 were nearly fully soluble in THF (> 96%), indicating that these are not strongly crosslinked, which is reflected in their thermogravimetric (TG) curves in Fig. 6. The fact that samples with greater crosslink density degrade more slowly at high temperatures is also proved by the TG curves for polystyrene and crosslinked polystyrene, presented in Fig. 8. Also, we can conclude that the processes used to isolate lignin to obtain samples LS2, LS4, and LS6 give easily THF soluble lignins than the commercial LS1 made by kraft process, indicating they are more homogenous than LS1.

Fig. 7 shows the TG curves for xylanase treated samples, wherein the xylan content of the lignins is minimal following removal of xylan by xylanase, leading to a carbohydrate-free lignin with more symmetric curves, as would be expected. The initial decomposition temperature

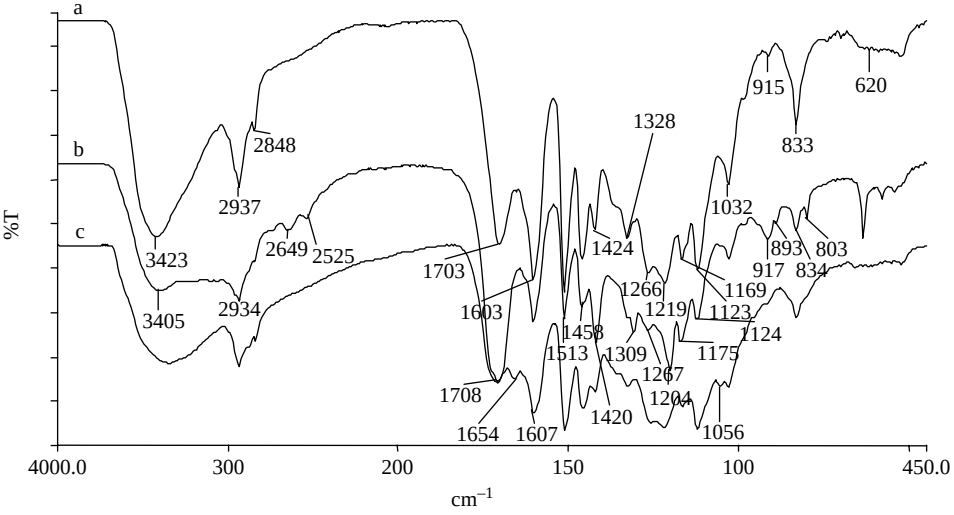

Fig. 4. FTIR of (a) organosolv lignin–carbohydrate complex LS2, (b) bagasse–lignin succinic acid adduct LS11, and (c) bagasse–lignin succinic acid–crown ether adduct LS12.

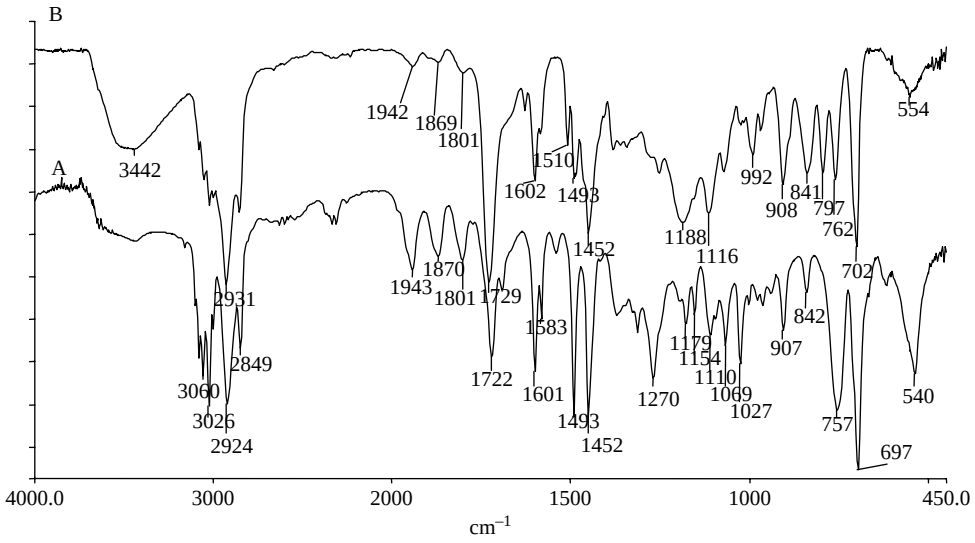

Fig. 5. FTIR of (A) polystyrene, and (B) styrene–divinylbenzene polymer.

and T_{max} of the two lignins (LS4, LS6) were found to be similar even though the isolation process was different; the marginal decrease in onset of degradation of LS6 over LS4 is due to its small sulfur content. These lignins are more stable than the commercial lignins studied (LS1). T_{onset} and T_{peak} of lignins were reduced after xylanase treatment. The reduction in T_{onset} may be due to chemical separation of carbohydrates from lignin–carbohydrate complex by the xylanase enzyme used for this purification treatment. The reduction in T_{max} may also be due to enzymatic fragmentation of the lignin molecule itself, which possibly causes structural changes in lignin (Fig. 8).

The TG of LS11 shows a sharp peak at 218 °C that could be due to the degradation of aliphatic chain of succinic acid introduced after reaction with lignin. From the TG curve (Fig. 9), it is seen that lignin succinate–crown ether is more stable at higher temperatures (due to crosslinking by stable amide bonds), whereas lignin–succinic acid adduct is unstable (greater aliphatic content). The TG of lignin succinate–crown ether shows more than 100 °C increase in T_{onset} and also an increase in the T_{max}, indicating increased crosslinking of the lignin by diamino DB 18-C-6. The degradation at 590 °C is also less than the other lignins studied. Thus the thermal analysis of various lignins provides evidence of their homogeneity, carbohydrate content, and extent of crosslinking.

3.8. HPLC studies

The lignin samples were analyzed by HPLC for their composition and purity. The HPLC were scanned at three different UV wavelength (1) 210 nm, (2) 254 nm and (3) 272 nm. Residual carbohydrates in the lignins are likely to be detected at 210 nm, while other chromophores will show up at the higher wavelengths. The results are shown in Figs. 10 and 11. It is clear from the HPLCs presented that carbohydrate removal from the lignins by xylanase treatment can be detected by HPLC at the lower wavelength 210 nm (HPLCs of LS4, LS5).

Based on the results, we can predict the structures of the lignins and lignin–carbohydrate complexes that can be obtained by varying the source of the biomass (softwood, bagasse, etc.), method of preparation (kraft process or steam process), and biochemical treatments such as xylanase for removal of residual carbohydrates. This would help to plan applications for the different lignin preparations. Our

Table 3
Thermogravimetric analysis (TGA) data for lignins, xylanase treated lignins and lignin derivatives under nitrogen atmosphere at heating rate of 10 °C/min

Sample	T_{onset} (°C)	T_{max} (°C)	Degradation (wt%)			
			240	350	T_{peak}	590
LS1	236	393	7	18	25.1	45.7
LS2	277	389	5.3	20.6	31	55.6
LS3	268	369	4	23	28.3	52.5
LS4	299	390	6.7	20	31	58
LS5	270	368	7.2	26.15	32	57
LS6	289	394	6.2	20	33.6	59
LS7	254	352	4.4	27.5	28	56
LS11	183	218 and 388	16.5	31	11.5 38.1	58
LS12	302	403	4.5	14	25.8	47.2

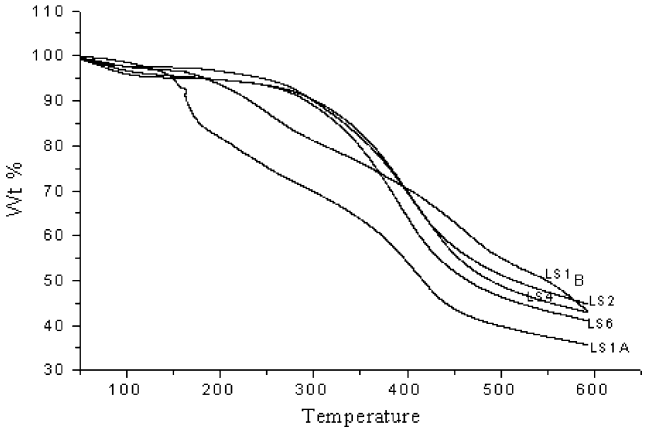

Fig. 6. Superimposed thermogravimetric (TG) curves of LS1B, LS1A, LS2, LS4, and LS6.

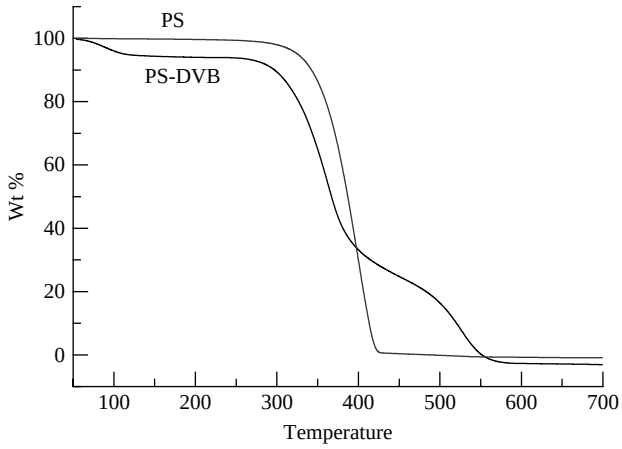

Fig. 8. TG of standard polystyrene and polystyrene-divinylbenzene (PS-DVB).

previous work (Galgali et al., 2002) has shown that functionalized polystyrenes, as model systems for lignins, can be made biodegradable by attaching as low as 1% by weight of carbohydrate moieties.

The schematic structures are shown in Figs. 12 and 13.

In conclusion, we have shown that a complex molecule like lignin–carbohydrate complex, consisting of a cross-linked hydrophobic aromatic structure linked to hydrophilic carbohydrate moeities (and its derivatives), is obtainable from different types of divergent sources and chemical isolation procedures. These polymers can have different structural parameters such as presence of lignin–carbohydrate linkages, different guaiacyl/syringyl ratios (wood and non-wood sources of the materials), sulfur linkages (or its absence) due to the isolation process used (such as kraft or soda process), effect of high degree of crosslinking (caused by reactions with diacids), etc. which can be detected by a combined study of FTIR, HPLC at various wavelengths with UV detector, TG, xylanase treatment, solubility and elemental analysis. The complexity of the molecule ensures that one cannot rely on a single spectroscopic method to discern the various facets of the molecule; rather an entire characterization protocol has to be in place to obtain a true picture of the lignin molecule. This detailed characterization is essential while developing diverse applications for this renewable biopolymer, available so abundantly but with limited commercial production. The presence of the carbohydrate linkages can be used for applications requiring greater extents of hydroxyl groups, such as polyurethane polymer systems, epoxy resin prepolymers, and so on. The residual carbohydrate units in lignins, thus not only make the product more economically viable, but also expand the range of its applications. We are doing further work on lignin–carbohydrate complexes by developing them as ingredients of new polymer composites, wherein the carbohydrate moieties will play a key role in anchoring the other components of the polymer system. The presence of the carbohydrate groups is likely to improve the biodegradability of these polymer systems. Our previous work (Galgali et al., 2002) has shown that functionalized polystyrenes, as model systems for lignins, can be made biodegradable by attaching as low as 1% by weight of carbohydrate moieties. The carbohydrate moiety, in addition to inducing biodegradability, also serves as reactive

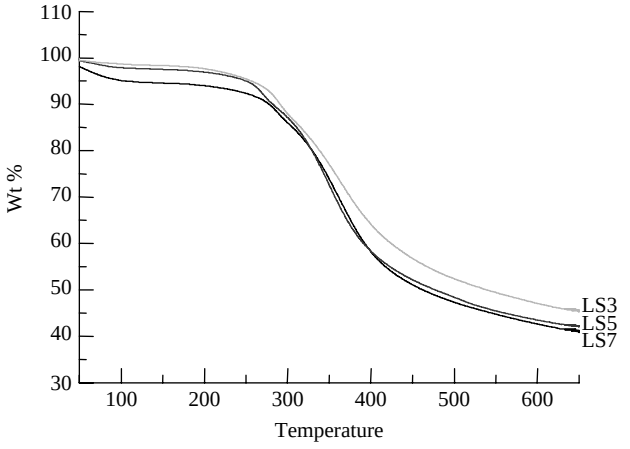

Fig. 7. Superimposed TG of xylanase treated lignins LS3, LS5, and LS7.

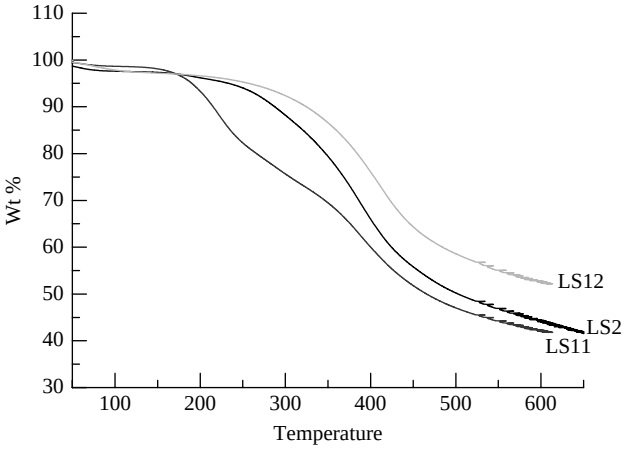

Fig. 9. Superimposed TG of LS2, LS11, and LS12.

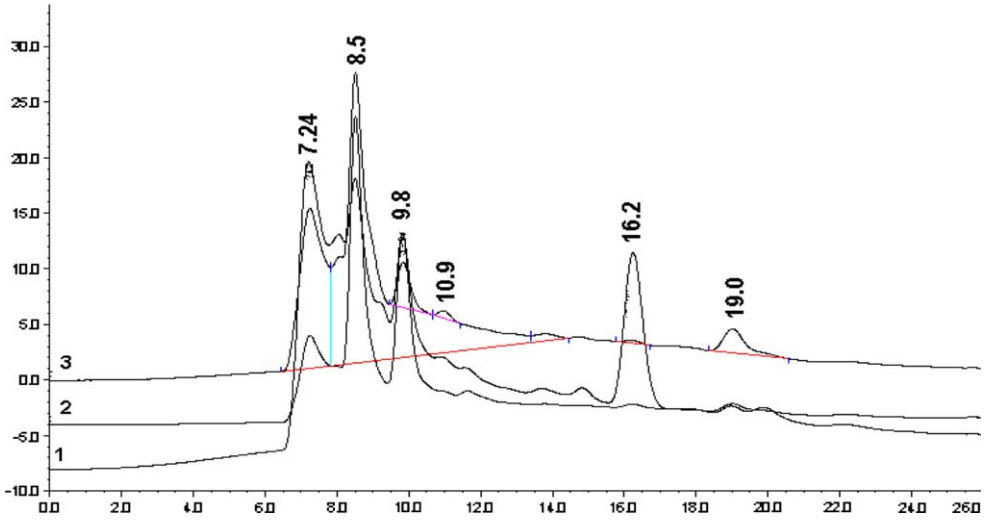

Fig. 10. HPLC of LS4 at (1) 210 nm, (2) 254 nm, (3) 272 nm.

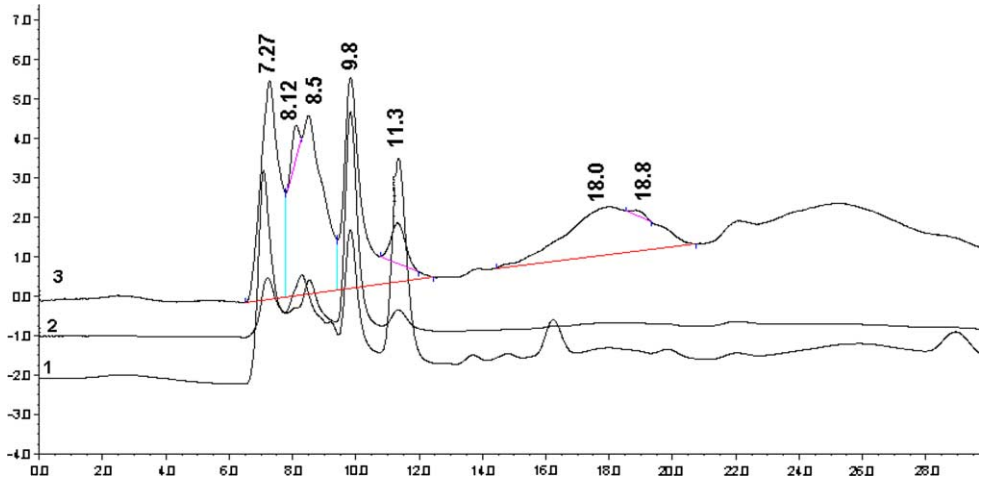

Fig. 11. HPLC of LS5 at (1) 210 nm, (2) 254 nm, (3) 272 nm.

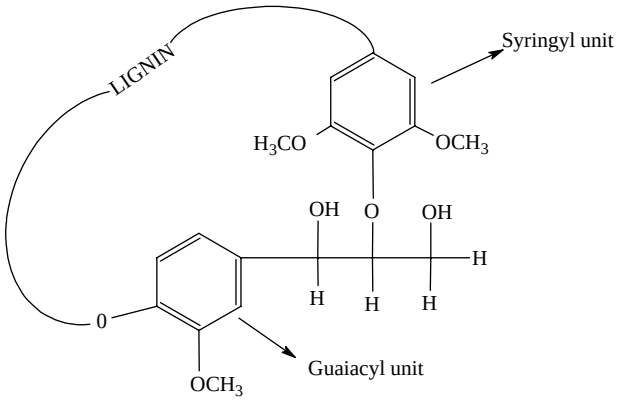

Fig. 12. Schematic structure of bagasse lignin without carbohydrate and sulfur content (after purification by xylanase enzyme).

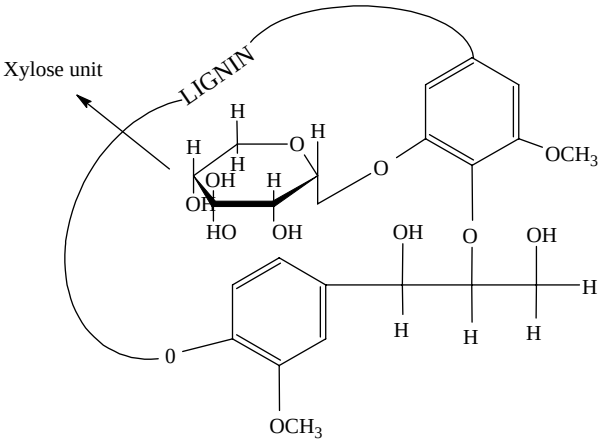

Fig. 13. Schematic structure of lignin–carbohydrate complex (e.g. LS2, LS4, LS6) obtained by steam-explosion or other processes.

site for anchoring other structural parameters to the polymer system. This area of work is gaining increased momentum with the present impetus to utilize renewable resources as well as develop biodegradable polymer materials.

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