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Thermochemical comparison of lignin separated by electrolysis and acid precipitation from soda black liquor of agricultural residues

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ABSTRACT

Lignin samples were separated from soda black liquor of wheat straw and bagasse by electrolysis and also by acid precipitation. These were compared for their thermochemical characteristics by ^{1}H NMR, TGA and DTA analyses. Lignins separated by electrolysis were found to have only 11–12 methoxyl groups per hundred phenylpropane units compared to 36–38 groups for acid precipitated lignins. They also had larger proportion of aromatic hydrogen and higher carbon to hydrogen ratio than acid precipitated lignins. All the lignin samples underwent a low temperature endothermic expulsion of adsorbed moisture. The distinctly exothermic nature of the thermal decomposition of acid precipitated lignins was missing for electrolytically separated lignins. Under comparable conditions, lignins separated by electrolysis could yield more amount of char compared to acid precipitated lignins.

1. Introduction

Lignin is an amorphous polyphenolic plant constituent [1,2]. It is one of the major polymers occurring in the plant kingdom; the second most abundant terrestrial polymer after cellulose [2,3]. It is generally obtained from black liquor, the spent stream obtained during the pulping of lignocelluloses [4]. Alkaline pulping currently is the most widely used method [5]. Traditionally, the lignin in black liquor has been used to derive energy while recycling the inorganics back to the digesters. But, this method is technoeconomically unviable for small paper mills and also causes air pollution [6]. In developing countries, like India, a sizable number of small paper mills use agricultural residues, like wheat straw and bagasse, as the raw material for producing pulp by the soda process.

However, there has been extensive research worldwide to find better uses for this lignin [5,7,8], commonly termed as alkali lignin. A great deal of research has been devoted to the development of lignin containing polymeric materials [3]. Lignin finds large application as a replacement of phenol in phenol-formaldehyde adhesives or resins [2,9]. It can be used as a natural polymer component in blends with other synthetic polymers [10]. With certain polymers, in suitable formulations, it can give partially or completely biodegradable composites [11]. Lignin can also be used as stabilizer in polymer formulations due to its antioxidant properties [3]. Lignin can be used as leather tanning material [12]. Another potential use of lignin can be due to its ability to stabilize oil water emulsions [13].

Lignin is able to give a large amount of char when heated at high temperature in an inert atmosphere [1]. This feature is the basic aspect for its use as flame retardant additives since char reduces the combustion rates of materials [14]. Lignin influences the thermal behaviour of polymer formulations in blends [15–17]. Owing to its high carbon content, lignin can be a starting material for preparing carbon fibers [18,19], films [20], and activated carbons [5,21,22]. Activated carbons from non-fossil sources are important from environmental considerations [23]. Being a potentially available waste from small paper industries transformation of lignin into activated carbons should be economically attractive.

Acid precipitation is the current most common method of recovering lignin from black liquor [2,24–28]. Precipitation can be carried out with mineral acids like sulfuric acid [29,30]. Precipitation with sulfuric acid upsets the liquor cycle chemical balance with excess sulfur [31]. Consequently, carbon dioxide is preferred for acidification [24,31,32]. Absorption of carbon dioxide from flue gases in place of purchased carbon dioxide has also been proposed [24,32,33]. The subsequent separation of lignin is an equally important step [28]. Filtration of the precipitated lignin is difficult owing to the gelatinous nature of the precipitate [34]. Research shows that organics can be separated from black liquor by electrolysis [35,36]. Since electrolysis of black liquor produces hydrogen at the cathode,

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this route for obtaining lignin from black liquor can be an attractive option [4].

However, the structure, and the consequent thermochemical properties of a particular lignin formulation depends on its botanical origin as well as the method of isolation [3]. In fact, no method of isolation gives a highly representative and totally unaltered native lignin [37]. The chemical characteristics and structural features of any lignin formulation are, therefore, dependent on its method of preparation. Consequently, lignin characterization is important to devise its optimal use [38]. Here, we present the thermochemical properties of lignin separated by electrolysis of soda black liquor of wheat straw and bagasse in comparison to that separated by acid precipitation.

2. Materials and methods

Black liquor samples used in the study were obtained from nearby mills. Samples were filtered through 400-mesh screen to remove any suspended matter. The original characteristics of the black liquor are shown in Table 1. Total dissolved solids in black liquor were estimated according to TAPPI standard test method T-650 pm-84. Organic to Inorganic Ratio in black liquor was determined according to TAPPI standard test method T-650 pm-84. Soda black liquors from agricultural residues have comparatively low organic/inorganic ratio owing to lesser delignification in soda pulping compared to kraft pulping. Electrolysis experiments were carried out in a Hoffmann voltameter with platinum anode and stainless steel cathode. Solids deposited on the anode were scraped off, washed thoroughly with distilled water and, dried. They were, then, dissolved in DMSO and filtered through sintered glass filter, with a pore size of 15–40 μm, to remove any inorganic impurities. Solids were then reclaimed by evaporation of solvent under vacuum and used for thermochemical characterization. Organics, as obtained above, were analyzed in their totality without further purification.

Acid precipitated lignin was separated from black liquor by acidification with 1 N HCl to pH 2.5. Precipitated solids were filtered, washed thoroughly with distilled water and dried. They were similarly dissolved in DMSO, filtered through sintered glass filter to remove any inorganic impurities, and reclaimed by evaporation of solvent under vacuum and used for thermochemical characterization without further purification.

^{1}H NMR spectra were obtained in DMSO-D_6 in a JEOL AL300 FTNMR spectrometer. Each spectrum was recorded with 32,768 data points, 5.2 μs pulse and pulse delay of 1.547 s. Simultaneous TGA and DTA analyses of samples were carried out in a PerkinElmer (Pyris Diamond) Thermoanalyzer. A typical sample mass of 10 mg was heated in alumina pans. Samples were heated from ambient to 800 °C at a heating rate of 10 °C/min. Samples were tested with nitrogen gas flow rate of 100 ml/min. 10 mg fine alumina powder was used as the reference. For DTA analyses the voltage drop at both ends of a differential chromel–alumel thermocouple were recorded, having one temperature probe embedded within the sample, while the other one was inside the reference. Solids were analyzed for their C and H elemental analysis in a VarioEL Elemental Analyzer by dry combustion. About 10 mg of sample was placed in the oxidative combustion chamber. During combustion, C and H are catalytically converted into carbon dioxide and water vapour, respectively. The gases so produced are separated as peaks. Integration of peak gives the concentration of elements. The percentage of oxygen was calculated by subtracting the C and H contents from 100%.

Table 1
Initial characteristics of black liquor.

	Total dissolved solids (%)	Organic/inorganic ratio	pH
Wheat straw	6.03	1.16	11.9
Bagasse	6.18	1.18	11.7

3. Results and discussion

3.1. ^{1}H NMR

Integration of the ^{1}H NMR regions, rather than the individually resolved peaks, has long been applied to estimate the different structural features in lignin formulations [39,40]. The ^{1}H NMR spectra of wheat straw lignin and bagasse lignin are shown in Figs. 1 and 2, respectively. Table 2 shows the hydrogen signal integrations subdivided into different structural regions [39–42]. From the elemental analysis of the samples (Table 3), these are assigned empirical formulae as presented in Table 4. Subsequently, the customary C_9 lignin formulae are worked out (Table 4) taking into account the total signal integrations for all protons, and those corresponding to methoxyl group. For example, wheat straw electrodeposited lignin (EDL) could be represented by an empirical formula, $C_{5.14}H_{6.73}O_{1.97}$. From Table 2, an area of 81.03 arbitrary units corresponds to 6.73 hydrogen atoms in the empirical formula. The area representing methoxyl group is 2.42 units which would be equivalent to 0.2 hydrogen atoms in the empirical formula. Since, in the methoxyl group, every carbon atom is associated with three hydrogen atoms, 0.2 hydrogen atoms would correspond to 0.07 methoxyl groups. The empirical formula could, then, be rewritten as $C_{5.07}H_{6.53}O_{1.9}(OCH_3)_{0.07}$, which in C_9 representation would be $C_9H_{11.59}O_{3.37}(OCH_3)_{0.12}$.

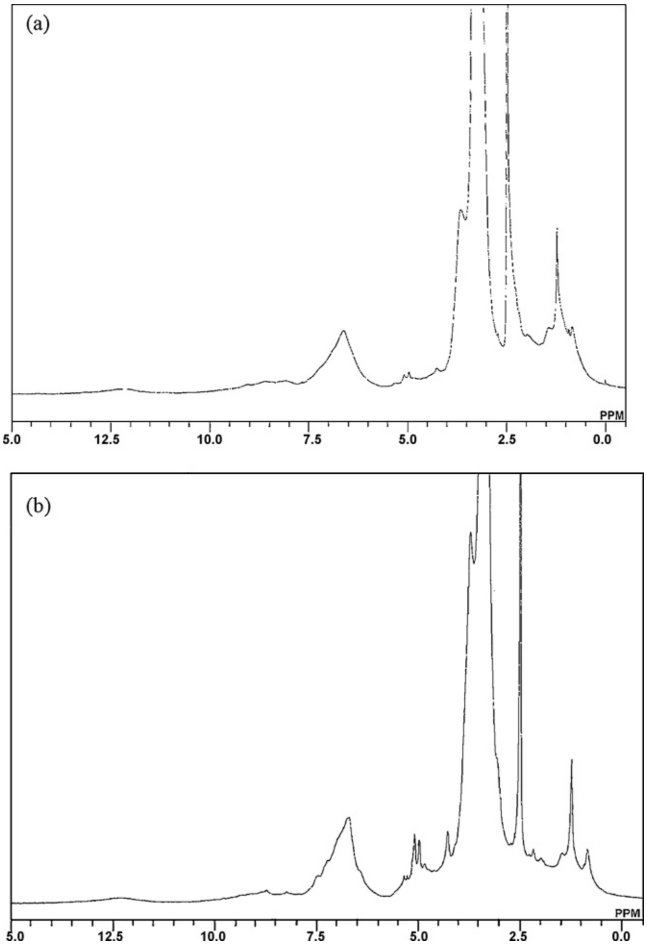

Fig. 1. ^{1}H NMR spectra of wheat straw lignin (a) EDL and (b) APL.

Table 2
^{1}H NMR signal integrations and assignments.

δ (ppm)	Signal integrations (arbitrary units)			
	Electrodeposited solids		Acid precipitated solids	
	Wheat straw	Bagasse	Wheat straw	Bagasse
6.25–7.9 (aromatic)	9.99	9.93	8.42	8.35
5.2–6.25 (benzylic)	0.37	0.49	2.58	2.71
3.55–3.95 (methoxyl)	2.42	2.23	4.96	4.75
3.95–5.2 and 2.5–3.55 (aliphatic)	60.13	59.14	58.07	57.69
<1.6 (non-oxygenated aliphatic)	8.12	7.39	2.81	2.70
Total	81.03	79.18	76.84	76.2

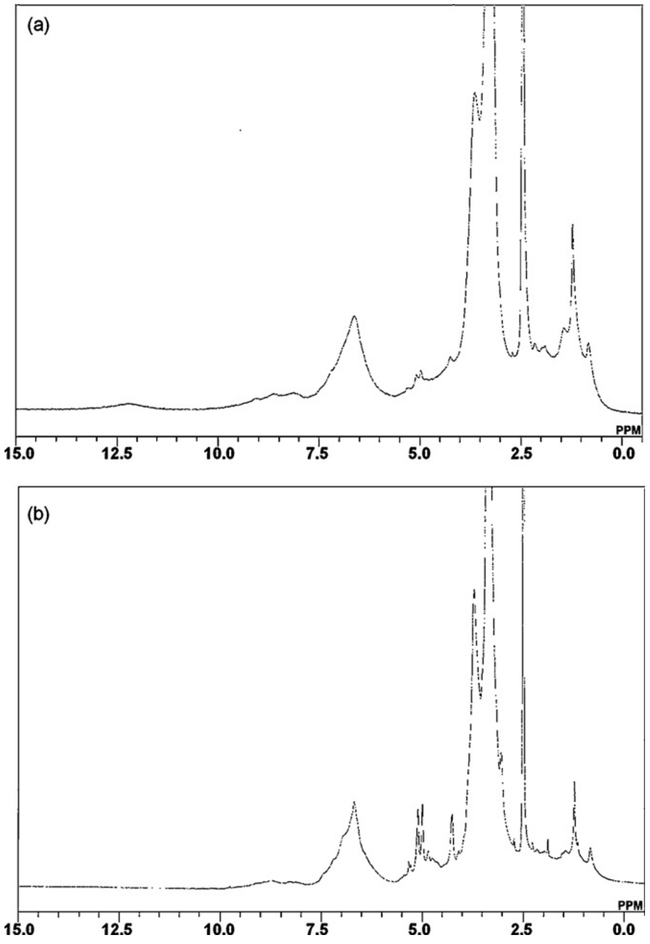

Fig. 2. ^{1}H NMR spectra of bagasse lignin (a) EDL and (b) APL.

Table 3
Elemental analysis of lignin samples.

Elements (% by weight)	Electrodeposited solids		Acid precipitated solids	
	Wheat straw	Bagasse	Wheat straw	Bagasse
C	61.69	62.19	53.07	52.76
H	6.73	6.36	8.48	8.37
O	31.58	31.45	38.45	38.87

From Table 4, it can be seen that EDL has lesser number of methoxyl groups compared to acid precipitated lignin (APL). In wheat straw, the APL has 38 methoxyl groups per 100 phenylpropane units whereas this number is only 12 for EDL. In bagasse, the APL has 36 methoxyl groups per 100 phenylpropane units in comparison to 11 methoxyl groups for EDL. Integration of ^{1}H NMR regions (Table 2) also reveals that EDL has larger proportion of aromatic protons compared to APL. This indicates lesser extent of substituent groups and linkages through the aromatic ring for EDL. APL also has a much higher proportion of benzylic hydrogen compared to EDL. These results are in conformity to the earlier findings [4]. Overall, the EDL, both from wheat straw and bagasse, has higher carbon to hydrogen ratio than the APL (Table 3).

Such differences should mainly arise from the distinctly different lignin separation mechanism in electrolysis compared to acid precipitation. Lignin separation from black liquor through acidification is primarily a coagulation phenomenon. In electrolysis, however, it is due to the selective anodic electroactivity of some of the organic anions present in the black liquor [36]. This is further exemplified by the vastly different lignin yields in the two methods. Acid precipitation of black liquor is well known to separate almost the entire amount of lignin present in it. In contrast, electrolysis of black liquor separates between 9% and 14% lignin present, as reported elsewhere [43].

3.2. DTA

The thermal transformations of wheat straw lignin and bagasse lignin are shown in Fig. 3. For both the black liquors the EDL underwent an initial endothermic transformation; the maximum peak temperatures being 70 and 75 °C, respectively, for wheat straw, and bagasse. This is due to the presence of adsorbed water and confirms to the results previously reported in literature [10]. The associated enthalpy changes were 139 and 210 mJ/mg, respectively. For wheat straw solids the transformation occurred between 29 and 145 °C whereas for bagasse solids this spanned from 33 to 158 °C. In addition, the EDL from bagasse black liquor exhibited two more endothermic transformations involving modest enthalpy changes of 12.8 and 12.1 mJ/mg. The first transformation was centered at 249 °C spanning from 215 to 282 °C. The second one occurred between 320 and 367 °C with the peak at 344 °C.

In comparison, the APL, from both the black liquors, had similar initial endothermic transformations. For wheat straw (Fig. 3(a)) it occurred between 32 and 149 °C, peaking at 69 °C, with an enthalpy

Table 4
Formula for lignin samples.

	Electrodeposited solids		Acid precipitated solids	
	Wheat straw	Bagasse	Wheat straw	Bagasse
Empirical formula	$C_{5.14}H_{6.73}O_{1.97}$	$C_{5.18}H_{6.36}O_{1.97}$	$C_{4.42}H_{8.48}O_{2.4}$	$C_{4.4}H_{8.37}O_{2.43}$
C_9 formula	$C_9H_{11.59}O_{3.37}(OCH_3)_{0.12}$	$C_9H_{10.86}O_{3.36}(OCH_3)_{0.11}$	$C_9H_{16.83}O_{4.71}(OCH_3)_{0.38}$	$C_9H_{16.7}O_{4.81}(OCH_3)_{0.36}$

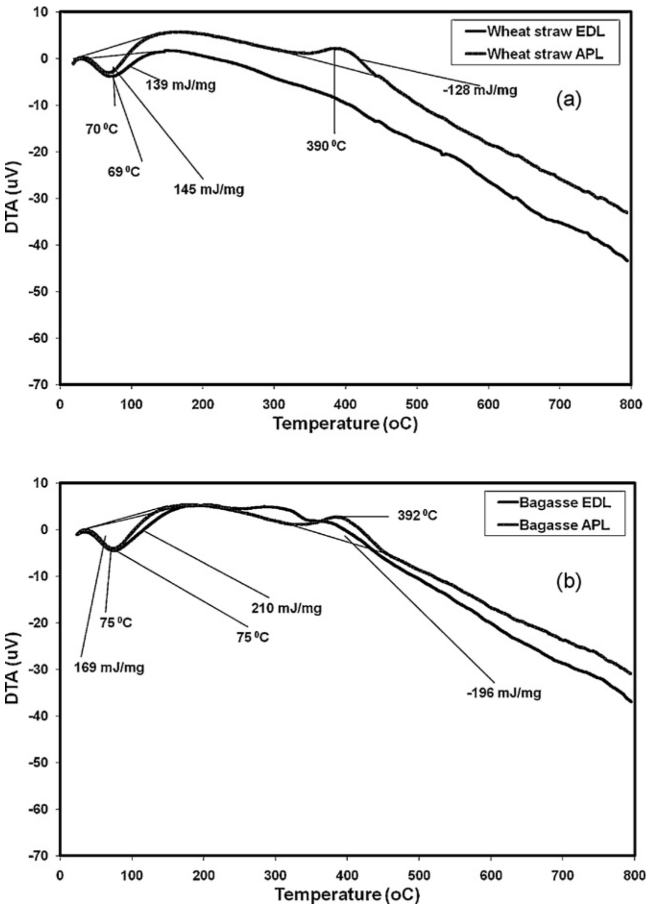

Fig. 3. DTA results (a) wheat straw lignin and (b) bagasse lignin.

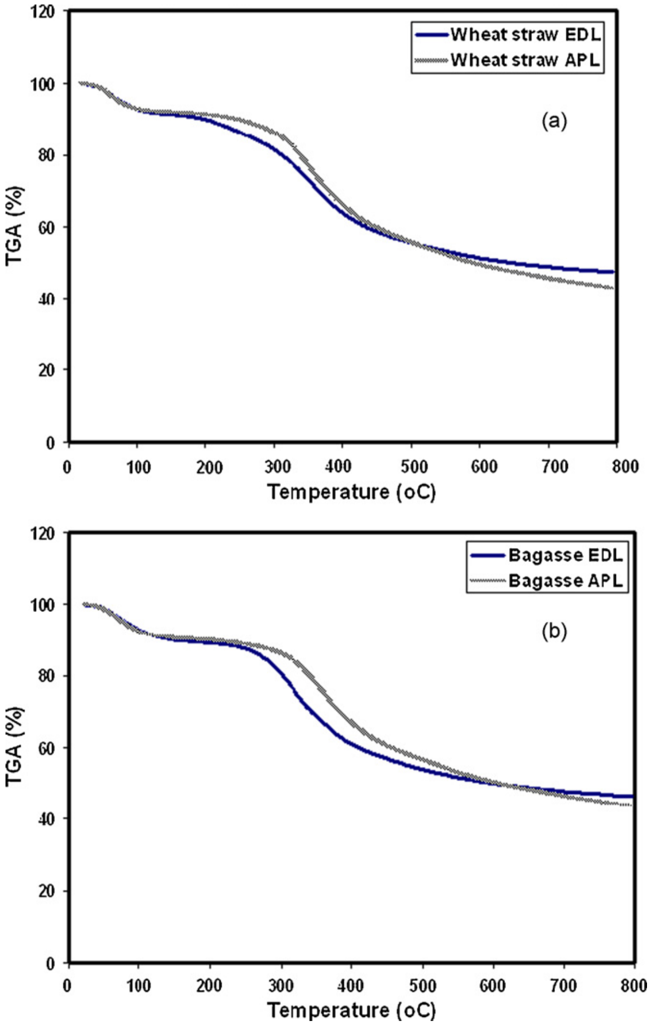

Fig. 4. TGA thermograms (a) wheat straw lignin and (b) bagasse lignin.

change of 145 mJ/mg. For bagasse (Fig. 3(b)), the transformation was observed between 36 and 160 °C with the peak at 75 °C and enthalpy change of 169 mJ/mg. However, upon further heating both the samples exhibited a pronounced exothermic transformation, which was totally absent in the case of EDL. For wheat straw this exothermic transformation, evolving 128 mJ/mg of energy, took place in the temperature range of 319–443 °C with the maximum at 390 °C. The similar transformation for bagasse evolved 196 mJ/mg of energy in the temperature range of 321–447 °C with the maximum at 392 °C. Such exothermic decomposition of lignin has been reported by other investigators for commercially available kraft lignin [23] and lignin precipitated from black liquor [44] and, therefore, is on expected lines.

3.3. *TGA*

Fig. 4 presents the TGA thermograms of wheat straw lignin, and bagasse lignin. The rates of thermal degradation are presented in Fig. 5. TGA results for the EDL samples show two distinct phases of weight loss. Initially, upon heating, the EDL from wheat straw black liquor underwent a weight loss of 8.65% with a maximum rate of 125.2 μg/min. at 67 °C. As can be seen, this initial loss in weight coincided with the endothermic peak of the DTA results, and was due to the expulsion of residual amount of moisture. Such moisture loss upon heating is normal in the case of lignins obtained from black liquor [7] as also for other types of lignins [10]. Similar results were observed for bagasse where the initial heating resulted in 9.02% weight loss with a maximum rate of 152.4 μg/min at 70 °C. Upon further heating, the wheat straw EDL had a profound thermal degradation between 250 and 450 °C accounting for 27.7% weight loss. The rate of this degradation peaked at 357 °C with the maximum rate being 227.2 μg/min. Beyond 450 °C the material continued to degrade at a much slower rate leaving a char residue of 47% at 800 °C. Similar behavior was observed for bagasse where the prominent thermal degradation between 250 and 450 °C accounted for 30.7% weight loss. The peak thermal degradation rate of 329.2 μg/min. occurred at 320 °C. Gradual thermal degradation continued above 450 °C and a char residue of 46.5% was obtained at 800 °C. For the EDL, both wheat straw and bagasse, the notable feature of the high temperature degradation was its largely athermic nature, as indicated by the DTA results.

Two distinct phases of weight loss upon heating is also evident for the APL. For wheat straw the initial expulsion of residual moisture, coinciding with the DTA endothermic peak, accounted for 7.21% weight loss with a maximum rate of 133.3 μg/min. at 63 °C. Similar transformation was observed in bagasse showing 7.59% weight loss and a maximum dehydration rate of 147.9 μg/min. at 70 °C. Upon further heating both the APL samples underwent thermal decomposition. For wheat straw, appreciable weight loss of 26.53% was noticed between 300 and 450 °C with a maximum decomposition rate of 271.7 μg/min at 357 °C. For bagasse, similar fast decomposition, accounting for 25.75% weight loss, took place in the temperature span of 300–450 °C. Decomposition rate peaked to 286.1 μg/min at 361 °C. However, in comparison to EDL, the high temperature thermal decomposition of APL was a distinctly exothermic phenomenon as indicated in the DTA thermograms.

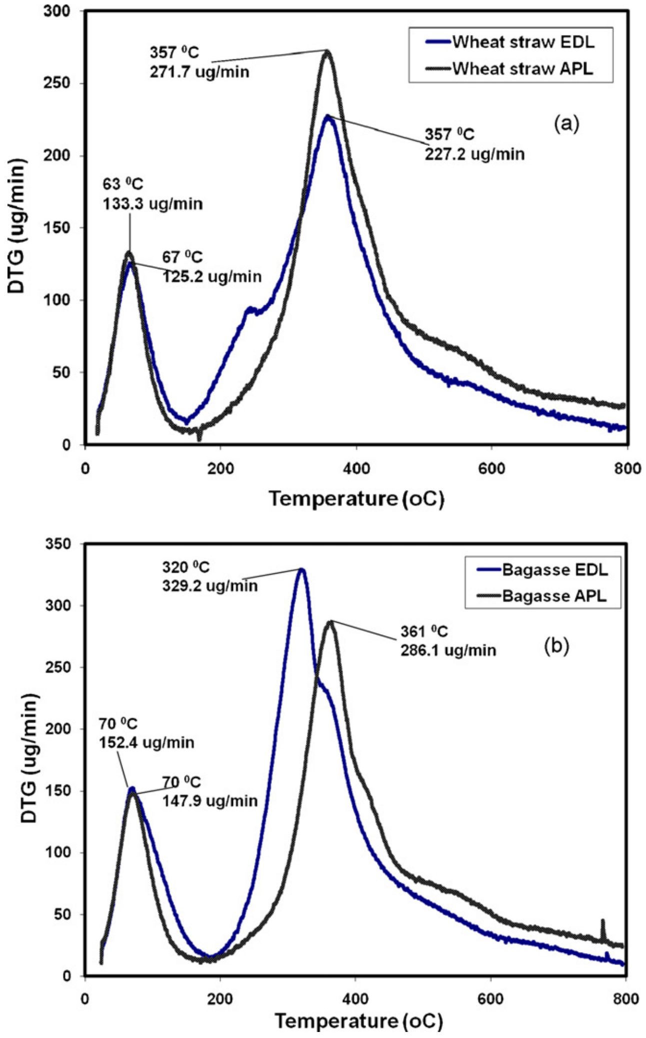

Fig. 5. Rate of thermal degradation (a) wheat straw lignin and (b) bagasse lignin.

For these solids gradual thermal degradation continued as they were heated past 450 °C leaving a char residue of 43% and 44%, respectively, for wheat straw and bagasse. APLs from black liquor are reported to yield 40–50% char upon similar thermal degradation [2]. Higher char residues obtained for EDLs are consistent with their higher carbon content (Table 3). As explained above, another reason could be the essential fractionation and possible rearrangement of lignin during electrolysis resulting in considerably lesser yields. This could also arise from the structural differences between EDLs and APLs as revealed by their ^{1}H NMR spectra as well as other spectroscopic studies [4]. Important among these are differences in the extent of substituent groups and linkages through the aromatic ring, especially the β–O–4 type entities [4]. Pyrolytic degradation of lignin is known to involve fragmentation of inter-unit linkages and formation of highly condensed aromatic structures leading to char residues [2,45].

4. Conclusions

Lignins obtained from agroresidue black liquors through electrolysis have distinct differences in molecular structure compared to the lignins obtained by acid precipitation. This reflects in their thermochemical characteristics. EDLs, with their higher carbon to hydrogen ratio, appreciably lesser methoxyl substitution, and lesser intermonomer linkages through the aromatic rings, behave differently during thermal decomposition. Their high temperature athermic decomposition leading to higher amount of char residues differs from that observed for APLs where exothermic decomposition leaves comparatively lesser amount of char. All these are significant in possible utilization of EDLs as precursors for carbon products.

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