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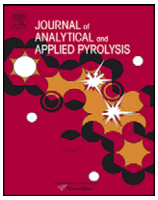

The behavior of kraft lignin during thermal treatment

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ABSTRACT

Purified kraft lignin fractions from technical pulping liquors of softwood and hardwood have been subjected to step-wise analytical pyrolysis in the temperature interval 200–900 °C. The heterogenic structure of kraft lignin was revealed by the formation of pyrolysis products throughout the entire temperature interval although the majority of products were formed at 500–600 °C. Beyond 700 °C, no further pyrolysis products could be detected but a substantial portion of the lignin was shown to be converted into thermally stable products (char) not accessible by analytical pyrolysis. With pre-oxidation of the lignin with air at 250 °C prior to pyrolysis, a shift towards higher pyrolysis temperature was observed with a concomitant change in product composition. Thermal gravimetric analysis on such lignins also showed an improved stability against degradation. Methylation of the lignin prior to pyrolysis did not induce any significant changes in behavior, except for much lower T_g values.

1. Introduction

The use of technical lignins such as kraft lignin as feedstock, for material systems like carbon fiber, adhesives or phenol-based polymers requires higher degree of purity and homogeneity than that of the original lignin. Thus, it has been shown that kraft lignin can be used in the production of carbon fiber provided that the lignin is sugar-free, ash-free and has a low degree of polydispersity [1,2]. When these prerequisites are fulfilled, kraft lignin from hardwood together with either a minor amount (5%) of synthetic polymer like polyethyleneoxide or polyethylene terephthalate or with added solvent-extracted low molecular mass kraft lignin can be used to produce carbon fiber with strength properties close to commercial carbon fibers made from petroleum pitch [3,4]. By solvent fractionation of softwood kraft lignin, it has also been shown that up to about 20% of a low molecular mass fraction can be used together with synthetic polyol and polymeric isocyanate for making polyurethanes with properties similar to those of commercial products [5]. In attempts to make phenol–formaldehyde resins, various purified lignins have been used as partial replacements for phenol with promising results [6–8].

In a previous work, it was shown that ceramic membranes can be used to achieve an "in line" purification of technical black liquors from kraft pulping of various wood species. Upon acidification according to the LignoBoost process [9] and further purification, virtually pure kraft lignin fractions having low degrees of polydispersity could be obtained [10]. However, by thermal gravimetric analysis (TGA) of the various isolated lignins, it was found that, irrespective of origin, a substantial loss of material (∼40%) took place in the temperature interval of about 200–600 °C with a maximum in material loss at about 400 °C. A similar result has been found in analysis of the change in elemental composition upon heating of purified hardwood kraft lignin [11]. Obviously, the heterogeneous structure of any lignin with a non-repetitive combination of interunit ether and carbon–carbon linkages and with a rather broad molecular mass distribution results in the facile release of substantial amounts of volatile products.

The nature of the material being volatilized at different temperatures has now been further characterized using analytical pyrolysis and thermal gravimetric analysis. Thus, by increasing the temperature step-wise by 100 °C in the interval of 200–900 °C and, at each temperature, subjecting the volatile products to analysis by GC–MS, a thorough description of the thermal behavior of kraft lignin from softwood and hardwood has been obtained. Furthermore, two different structural modification reactions of the lignin have been evaluated, viz. oxidation by air (oxygen) and blocking of phenolic hydroxyl groups by methylation prior to fractionated pyrolysis. The former type of treatment is similar to that applied on polyacrylonitrile (PAN) or pitch fibers prior to carbonization to carbon fiber [12] and has also been applied on both acetic acid [13] and on kraft lignin fibers [1] in order to obtain stabilization against fiber fusing upon heating. Methylation of phenolic hydroxyl groups, on the other hand, was done with the purpose of

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preventing assumed radical-induced condensation of aromatic nuclei during heating [14]. An increased fusibility of the lignin should be expected.

2. Experimental

2.1. Materials

Industrial kraft lignins originating from birch (Hardwood Permeate lignin; denoted HP15), eucalypt (*E. globulus*) (Eucalypt Permeate lignin; denoted EP15), softwood (pine/spruce) (Softwood Permeate lignin; denoted SP15) and high yield softwood pulping (Liner Permeate lignin; denoted LP15), were used. The black liquors were ultra-filtrated through a 15 kDa membrane, and the permeate lignins were isolated as described before [10]. As references, milled wood lignin (MWL) from birch and spruce with a methoxyl content of 17.6% and 15.0%, respectively, were used. For comparison, polyacrylonitrile (PAN), purchased from Aldrich, the polymer normally applied in the production of carbon fibers, was studied with thermal gravimetric analysis.

2.2. Methylation

About 100 mg of lignin was accurately weighed in a stainless steel reactor equipped with a screw cap. A tenfold excess of 1,4-diazabicyclo[2.2.2]octane (DABCO) relative to the lignin hydroxyl groups was added together with a twofold excess of dimethyl-carbonate (DMC). The mixture was heated for 7 h at 180 °C and cooled. Acetone:water (7:3) was added to completely dissolve the lignin. After evaporation of the acetone and further addition of water, the lignin was separated by centrifugation and washed. The lignin was suspended in water and isolated by freeze drying. All recovered lignin was fully methylated as revealed by FTIR analysis (lack of hydroxyl groups).

2.3. Thermal stabilisation

About 50 mg of lignin was accurately weighted in a carborundum ship and placed in a tube furnace type 30-50/15-VL, Entech, Sweden. The temperature was increased to 250 °C at 0.5 °C/min and left for 60 min in air (oxygen) or nitrogen atmosphere. The temperature was decreased by 3 °C/min to 90 °C, and, thereafter, the sample was allowed cooling down to room temperature.

2.4. Thermal gravimetric analysis

Thermal gravimetric analysis was performed using 2–8 mg samples to determine the mass loss during heating. The sample was dried at 105 °C for 20 min before it was heated to 1000 °C at a heating rate of 15 °C/min. The sample purge gas (helium) had a flow rate of 20–35 mL/min, and the balance purge gas (nitrogen) flow rate was 40–60 mL/min. A PerkinElmer TGA7 instrument was used for the measurements.

2.5. Pyrolysis-GC–MS

Pyrolysis was performed using a filament pulse pyrolyser (PYROLA 2000, Pyrol AB, Lund, Sweden) coupled to a GC/MS system. The latter consisted of a gas chromatograph from Fisons Instrumental (GC 8065) and a mass spectrometer from Fisons Instrumental (MD800 Quadrupole). The capillary column used was a BPX5 low bleed/MS; 30 m in length, 0.25 mm i.d. and with a film thickness of 0.25 μm (SGE- Chrompack). The temperature program was: 60 °C for 1 min, 19 °C/min to the final temperature 300 °C and hold for 10 min. The mass spectrometer was operated in electron impact mode (EI, 70 eV, $m/z = 20–450$). All lignin samples were evaluated with fractionated pyrolysis starting at 200 °C and increasing the temperature in 100 °C increments to 900 °C. For specific analysis of very volatile compounds, the capillary column used was a CP-Sil 5 SCB WCOT; 60 m in length, 0.32 i.d. and with a film thickness of 8.0 μm (Varian). In addition, the four different kraft lignins as well as the reference native lignins were pyrolyzed and analyzed at 600 °C. Most pyrolysis products were identified based on published mass spectra [15] and with numbering based on increasing retention time in the gas chromatographic separation.

3. Results and discussion

3.1. Analytical pyrolysis of lignins

Lignins are well suited for analysis by pyrolysis, and the technique as well as the various instrument set-up arrangements has been thoroughly described in the literature [15]. Most of the work so far has, however, dealt with the pyrolysis of either isolated native lignins or of wood and other biomass materials [15–17]. A few examples on the analytical pyrolysis of kraft pulp fibers and of the corresponding dissolved lignins can be found [18,19]. In addition, some work has been done on the mechanisms of pyrolytic degradation by the use of selected model compounds for lignin [20–22].

In the present work, two different reference lignins were used, viz. isolated native lignin (MWL) from spruce and birch. These were pyrolyzed at 600 °C and the products separated and identified by means of GC/MS. Relative peak areas were calculated as a percentage of the sum of all peak areas from lignin fragments. In a similar way, the kraft lignins from high-yield (liner) softwood pulping (LP15), softwood pulping (SP15), birch pulping (HP15) and *E. globulus* pulping (EP15) were analyzed. In all experiments, a remaining amount of material was found in the sample holder after pyrolysis, suggesting that a portion of the lignin was chemically modified to form thermally stable structures and/or char.

The pyrolysis data are presented in Table 1 and show that the comprehensive changes in lignin structure known to occur during kraft pulping can be readily visualized by pyrolysis. Thus, for both softwood and hardwood lignin, major changes in the intensity of several prominent peaks are evident. An increase in guaiacol (softwood) or syringol (hardwood) is illustrative of the formation of new end-groups due to cleavage of β-O-4 structures, whereas the increase of 4-methylguaiacol or 4-methylsyringol and a corresponding decrease of vanillin (syringaldehyde) show that the number of oxygenated side-chain α-carbon atoms has decreased during pulping. Other major changes include the decrease or complete absence of lignin end-groups such as coniferyl (sinapyl) alcohol and conifer-(sinap-)aldehyde. All observations are well in line with other analytical methods for lignin before and after kraft pulping [23].

In order to obtain more accurate information about the material loss in lignin on heating to different temperatures, step-wise pyrolysis was performed on each of the kraft lignins in the temperature interval from 200 to 900 °C. In all cases, only minute amounts of material, mostly guaiacol or syringol, were released at either 200 or 300 °C, as shown in Fig. 1 and detailed in Table 2 for SP15 and in Table 3 for HP15. Upon increase of the temperature to 400 °C, the two hardwood lignins were found to release substantial amounts of phenols, and at 500 °C, a maximum in the release of material was found. No loss of material could be detected at 700 °C or higher, however. For the softwood lignins, on the other hand, a somewhat higher maximum temperature for the release of material was evident with major formation of products both at 500 and 600 °C, whereas the loss at 400 °C was small. For these lignins, formation of minor amounts of identifiable compounds