

PRODUCTION OF CARBON MATERIALS FROM BIOMASS

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INTRODUCTION

Lignin is the most abundant renewable aromatic polymer. There is an abundance of lignin residues produced as a byproduct of pulp and papermaking which have a fuel value of between \$0.00 and \$0.04 per pound (1). The size of this resource can be appreciated by considering that the total amount of lignosulfonates and kraft lignin together outweigh the sum of all manmade polymers in the United States (2). Given the relatively low cost, high abundance, and renewable nature of this resource, it is not surprising that many attempts have been made to develop higher value products from lignin (1,3,4).

Carbon materials are a much higher added value product than almost any other use of the products which can be produced from lignin. This is especially true in the case of carbon fibers. Carbon fibers are becoming increasingly important as components of composite materials due to their unique chemical and physical properties (5). The finished fibers can sell for tens to hundreds of dollars per pound, so the potential exists for a large premium to be paid for a feedstock which could result in lower manufacturing costs or superior fiber properties. Consequently, the development of processes which can utilize lignins for this purpose and the production of other high value carbon materials has the potential for a high payoff. It would also result in the utilization of lignin as a raw material for a high technology, internationally competitive industry.

EXPERIMENTAL

Sample Selection - A set of eight different lignin samples was examined. The lignin samples and their sources are listed in Table 1. The first six samples were used in a previous project (6) and the last two were obtained specifically for the current project (7).

Table 1 - LIGNIN SOURCES

<u>Lignin</u>	<u>Wood</u>	<u>Manufacturer</u>	<u>Pre-Treatment</u>
Iotech	Aspen	Iotech Corp. ^a	Steam explosion
Stake (ST)	Aspen	Stake Tech. Ltd. ^a	Autohydrolysis
BEC	Aspen	Biological Energy Corp. ^b	-
Indulin I	Pine	Westvaco ^c	-
Ethanol (ET)	Aspen	d	Steam explosion
H ₂ SO ₄	Aspen	d	Steam explosion
SE	Poplar	VPI	Steam explosion
RTI		Repap Technologies	Ethanol/water Extraction

Notes for Table 1

- a. Extraction in dilute basic solution followed by precipitation with dilute acid.
- b. Wood chips are cooked with an ethanol-water solution in an autoclave at 130°C for 30-90 minutes.
- c. Wood is cooked with a 10% solution of 80/20 volume % sodium hydroxide/sodium sulfide. Trade name is Indulin ATR-CK1.
- d. Prepared by Eitan Avni at the University of Connecticut from wood steam exploded by Iotech Corp.

The lignin samples were chosen to represent a range of wood types and preparation methods.

Experimental Approach - The production of carbon materials from lignin is made difficult by the fact that it is highly substituted with oxygen functional groups. This makes the material too reactive toward crosslinking reactions for the formation of anisotropic carbons. These groups must be removed without removing much of the aromatic material which is desirable for the production of carbon materials. The approach taken in this study was to first pyrolyze the lignins to produce a tar and then to thermally and/or catalytically treat the tars to produce a material which could be a substitute for mesophase pitch produced from petroleum. The basis for this approach was previous work done on coal tars which suggested that secondary pyrolysis of tars would reduce the amount of functional group substituents and reduce the average molecular weight (8-11). In order to implement this approach, a two-stage reactor system was developed, as described below and in Ref. 7.

Two-Stage Fixed-Bed Reactor - The lignin pyrolysis/tar cracking experiments were done in a reactor with two separate pyrolysis zones with independent temperature regulation capabilities and with the ability to monitor the product tars on-line with FT-IR spectroscopy (see details of TG-FTIR software-hardware principles discussed below) using an IBM IR-40 spectrometer. A portion of the product stream is extracted out through a filter by means of a peristaltic pump through a line which bypasses the multi-pass cell. The tar component of the products which collected on the filter (cotton wool) was washed out with acetone, dried, weighed and used for further analysis. Helium was used as the carrier gas and the best reproducibility was achieved at pumping rates which resulted in 10-30% extraction of the tar.

The typical experimental conditions were as follows: sample weight: 0.15 ± 0.05 g; He flow: 0.47 liter/min, cm^2 (inner tube I.D. is 0.7 cm). The heating rate (upper chamber) was 30°C/min. (max. temp 780°C) and the secondary pyrolysis (lower chamber) temperature was kept constant during the whole experiment at temperatures ranging from 400 to 700°C. The carbon content of the tar deposited on the wall of the inner tube or on the catalyst surface was measured by replacing the He flow with O_2 . The upper and lower chamber temperatures were raised up to 700°C separately to achieve complete combustion and the CO_2 and CO measured.

This reactor was used primarily for experiments where lignin was pyrolyzed in the first stage at a constant heating rate and the tars were passed to an isothermal second stage. Experiments with both the second stage empty and filled with a catalyst bed were done.

Catalyst Selection - The catalyst examined in the second stage was Alcoa (Type F-20) chromatographic grade 80-200 mesh activated Alumina (EM Science). Glass wool was used to support the catalyst particles. Other catalysts, such as calcium oxide, were considered but good results were obtained initially with alumina and it was used for the remainder of the study. The alumina was chosen because it has a high affinity for polar materials and the goal was to selectively remove oxygen functions from lignin tar. It is also a material which can easily be regenerated once coke formation has occurred.

RESULTS

Lignin Characterization Experiments - A series of lignin screening experiments was done to see how many lignins would be suitable candidates for this approach. These experiments were done in a TG-FTIR system developed at AFR (12,13). The apparatus consists of a sample suspended from a balance in a gas stream within a furnace. As the sample is heated, the evolving volatile products are carried out of the furnace directly into a 5 cm diameter gas cell (heated to 150°C) for analysis by FT-IR. The FT-IR can obtain spectra every 0.2 s to determine quantitatively the evolution rate and composition of several hydrocarbon compounds. The system allows the sample to be heated on a pre-programmed temperature profile at rates between 3°C min⁻¹ and 100°Cs⁻¹ up to a temperature between 20 and 1000°C and held for a specified time. The system continuously monitors: 1) the time-dependent evolution of the gases (including specific identification of the individual species such as, CH₄, C₂H₂, C₂H₄, C₂H₂, C₃H₄, benzene, etc.); 2) the heavy liquid (tar) evolution rate and its infrared spectrum with identifiable bands from the functional groups and 3) weight of the non-volatile material (residue). An analysis of C,H,N and S in the residue at the end of the pyrolysis experiment can be obtained by introducing oxygen to burn the residue and analyzing the combustion products.

As an example of the analysis procedure, the pyrolysis of the lotech lignin is described. Figure 1 illustrates the weight loss from this sample, the sum of the evolved products, and the temperature history. A 20 mg sample is taken on a 30°C/min temperature excursion in the helium sweep gas, first to 150°C to dry for four minutes and then to 900°C for pyrolysis. The evolutions of gases derived from the IR absorbance spectra are obtained by a quantitative analysis program that employs a database of integration regions and calibration spectra for different compounds (12,13). Figures 1b through 1f illustrate the evolution rates and integrated amounts evolved for Tar, CH₄, H₂O, CO₂ and CO, respectively. Because the data are quantitative, the sum of the evolved products matches the weight loss as determined by the TGA balance (Fig. 1a).

The results from a standard (30°C/min) TG-FTIR analysis of the eight lignin samples are summarized in Fig. 2. The tar yields from the eight samples ranged from ~10 wt. % tar for the H₂SO₄ lignin to > 50 wt. % for the lotech lignin. A number of the lignins gave relatively high tar yields (>30 wt. %), so it appears that the generation of primary lignin tar by pyrolysis is a good starting point. An especially interesting sample was the Repap Technologies (RTI) lignin. This sample is produced in large quantities as a byproduct of a proposed organosolv pulping process.

The amount of tar formed was sensitive to the heating rate of the primary pyrolysis stage and to the bed depth (7). The results suggested that the highest yields of tar would be obtained in a dilute phase, entrained flow pyrolysis experiment. This is similar to what has been observed in the case of coal pyrolysis (14).

Experiments In Two-Stage Reactor - A series of experiments was done in the two stage reactor with an alumina catalyst with two of the lignins (SE and RTI) over a range of second stage temperatures (400-700°C). The results from the on-line absorbance measurements are shown for the RTI lignin for various cases in Figs. 3 and 4. For both lignins, a significant reduction in oxygen functions was observed in the on-line FT-IR spectra of the tar when the catalyst (alumina) is present, but not when it was absent.

The IR spectra of both the SE and RTI lignin are very similar and the oxygen containing functional groups appear at 1215, 1107 and 1060 (C-O) cm^{-1} as well as 1607 (C=O) cm^{-1} . To characterize the polar nature (oxygen content) of a tar we use the parameter

$$PI = \frac{\frac{A(1215)}{A(1508)} + \frac{A(1107 \text{ or } 1060)}{A(1508)}}{2}$$

where A (ν) is the peak height of the νcm^{-1} peak and PI is a polarity index. The smaller the value of PI, the less oxygen the tar contains and the better it might be as a precursor for carbon materials.

Figure 5a shows PI for the main tar evolution peaks for SE and RTI lignins. Figure 5b shows the corresponding results for the tar yield and deposit formation. These results show that relatively high yields of tar can be obtained at high oxygen removal efficiencies, with relatively low deposit formation. The optimal temperature for operation of the second bed was about 550°C.

CONCLUSIONS

The preliminary conclusions of this work are as follows:

- o A set of eight lignins was characterized using the TG-FTIR programmed pyrolysis system. The amount of tar produced in a standard 30°C/min. pyrolysis of most of the lignins was about 35-50% on a dry basis. The amount of tar produced was found to be sensitive to heating rate and bed depth. Higher heating rates produced higher tar yields while larger bed depths produced lower tar yields.
- o A thermal treatment of the tars in the second stage does not significantly degrade the oxygen content.
- o The presence of activated alumina does significantly and selectively catalyze the decomposition of oxygen functional groups in the tar based on the on-line FT-IR analysis. The main gaseous products of the tar decomposition are CO, CO₂ and CH₄.
- o The activity of the alumina appears to be a maximum for oxygen removal at - 550°C. The loss of tar under these conditions is about 40%.
- o The net yield of modified tar from the current system appears to be - 15% for SE lignin and 20% for RTI lignin under the best conditions. This may be improved by an entrained bed reactor system for the primary pyrolysis stage.

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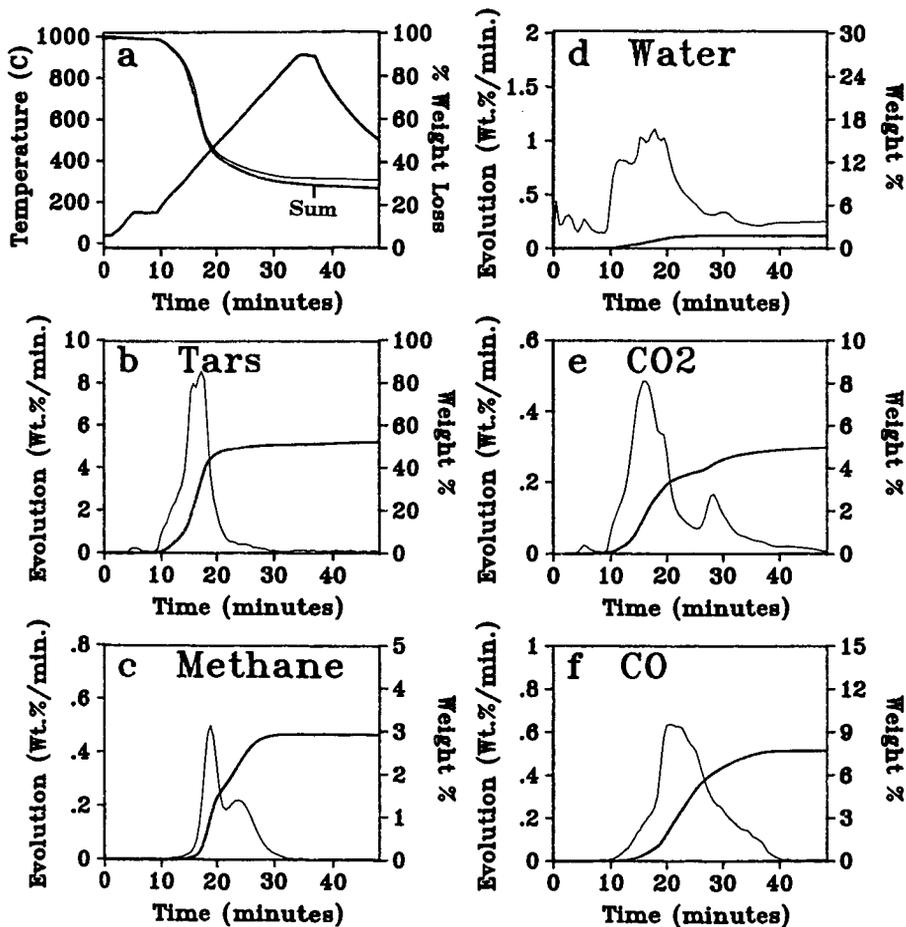


Figure 1. TG-FTIR Analysis of Iotech Lignin at 30°C/min.

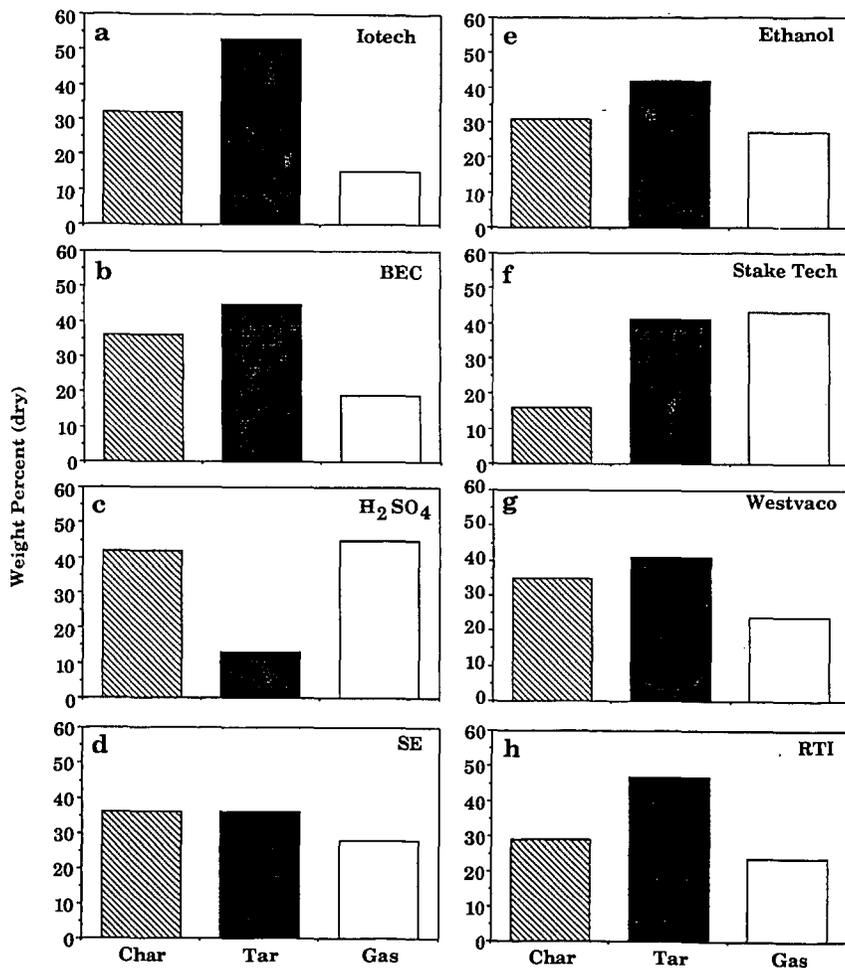


Figure 2. Comparison of Char, Tar and Gas Yields from Programmed Pyrolysis of Eight Lignins.

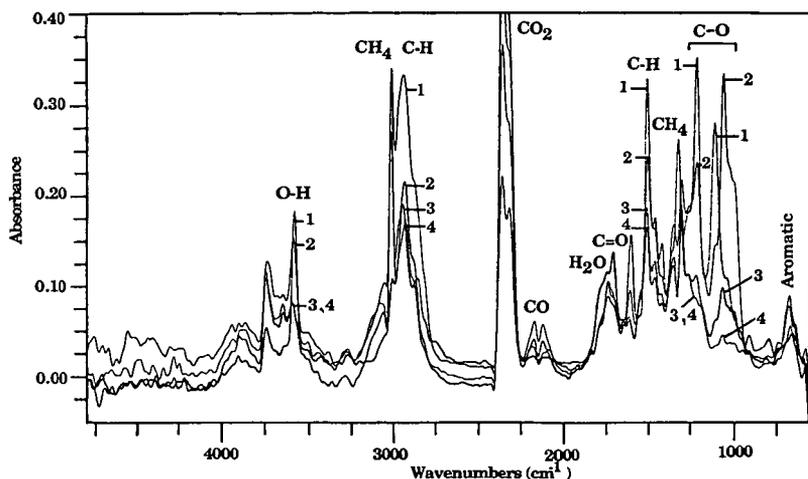


Figure 3. On-Line Tar Spectra from Experiments in the Two-Stage Fixed-Bed Reactor with RTI Lignin. Case 1 = 400°C, No Catalyst; Case 2 = 400°C, with Catalyst; Case 3 = 550°C, with Catalyst; and Case 4 = 600°C, with Catalyst.

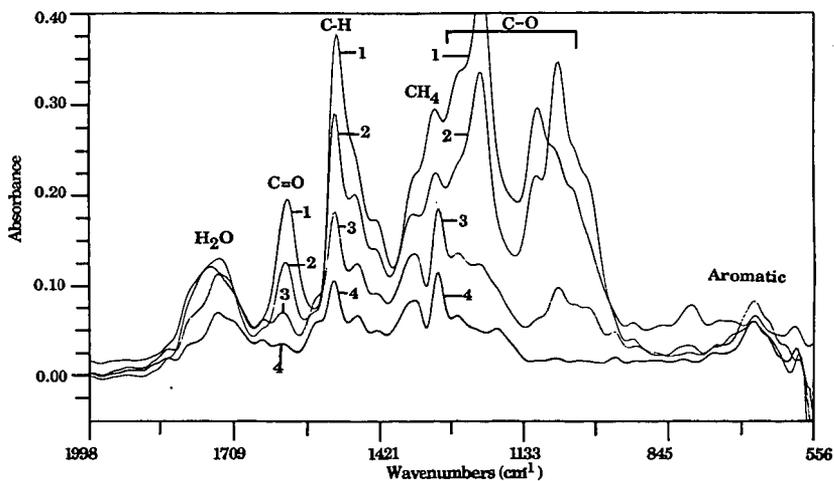


Figure 4. Expanded View of Spectra in Fig. 3.

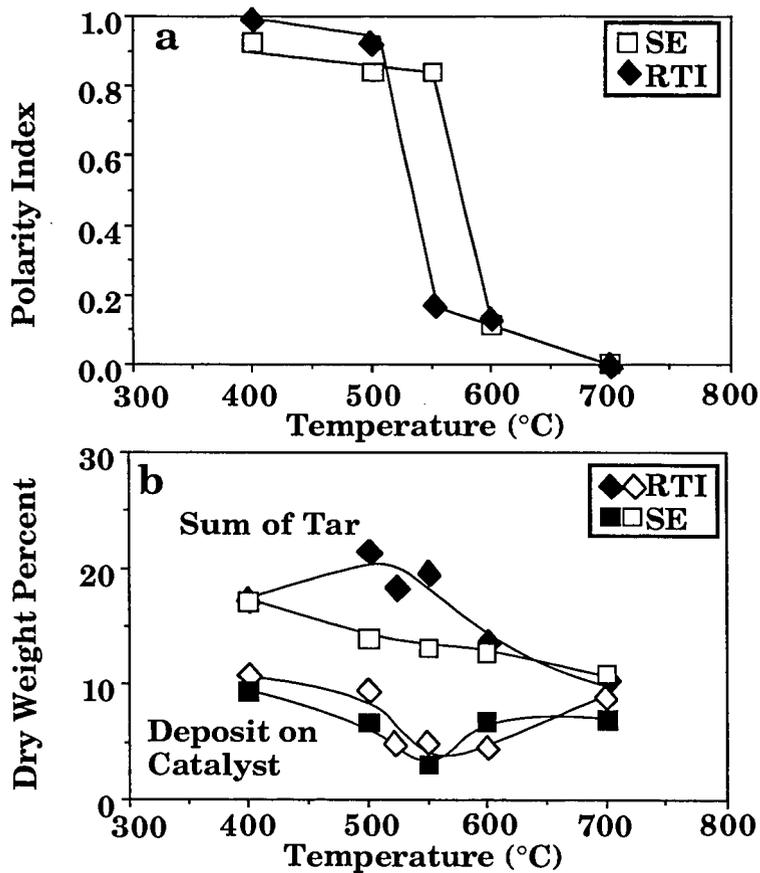


Figure 5. Effect of Lignin Type and Temperature on a) Tar Polarity Index and b) Tar Yield (◆, □), Deposit Yield (◇, ■).