



INVESTIGATING PYROLYSIS CONDITIONS OF COALS FOR CARBON FIBER PRODUCTION

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Introduction

With the decreased use of coals for energy generation, many are trying to find alternative applications for this valuable resource. Carbon fiber (CF) production has been increasing over the last few years and is primarily used in the aerospace and defense industries, with increasing application in wind energy, sporting goods, and automobiles¹. There are two main types of CF: PAN-based and coal tar pitch (CTP) based. CTP-based CF is typically made from mesophase pitch, rather than isotropic pitch, due to its high modulus, thermal conductivity, electrical conductivity, or low coefficient of thermal expansion properties². Mesophase pitch-based CF is more desirable due to its superior properties; however, it is more expensive to produce, and it is only produced as a by-product of commercial coking processes. Currently, non-coking coals are not typically used for creating mesophase pitch-based CF, and these coals constitute more than 50% of coal production in the US³.

Non-coking coals are typically lower in rank and usually have much higher concentrations of aliphatic and oxygen-containing functional groups, which makes them poor for coking. Our group is interested in learning how to create mesophase CTP from traditionally non-coking coals. We aim to utilize secondary pyrolysis reactions to "fine tune" the coal tar products towards a CTP capable of forming mesophase. We will focus on varying secondary pyrolysis gas phase residence time to examine its effect on improving mesophase growth in CTP. The primary coal we are working with is a bituminous Utah Sufco coal, after which we also intend to do future testing on other non-coking coals.

Materials and Methods

Pyrolysis of the Utah Sufco coal was performed in a two-stage, fixed-bed reactor. The coal bed was placed in the first reactor where it was pyrolyzed at 700°C, after which the pyrolysis vapors were passed into the second stage and subjected to homogeneous secondary gas phase reactions at 900°C. The tar vapors were condensed and captured in a set of collection jars and impingers. The two-stage reactor allowed gas phase residence times to be varied between 1 – 18 seconds. The coal tars were dissolved and filtered with tetrahydrofuran to remove any coke or other impurities. After filtration, the coal tars were distilled and heat soaked in a stainless-steel sparging reactor at 425°C for 3 hours to create a mesophase CTP. Specific coal tar samples will be hereafter denoted as U-CT-X, where X is the average residence time of the tar in the gas phase in seconds, and the respective heat-soaked pitch samples will hereafter be denoted as U-MCTP-X. Two commercial coal tar pitches are compared with our created CTP's. CTP-A is a refined commercial CTP from an industrial coking process and CTP-B is an unrefined by-product of a coking process using coal blends.

The coal tars were characterized by using Fourier transform-infrared spectroscopy (FT-IR), nuclear magnetic resonance spectroscopy (NMR), and matrix-assisted laser desorption ionization mass spectroscopy (MALDI-MS), while the heat-soaked samples were further characterized by polarized microscopy.

The tar samples were analysed in the FT-IR by placing the samples directly on the ATR crystal window to maximize contact. For the NMR analysis, the tar samples were dissolved as a 3 wt% solution in deuterated chloroform (CDCl₃) with 1% v/v of tetramethylsilane. Proton NMR (¹H NMR) was performed on all tar samples to quantify protons of interest, while ¹H-¹³C heteronuclear single quantum coherence (HSQC) NMR experiments were performed on just two samples to date in order to learn more information about hydrogen donor proton chemical shifts. For the MALDI-MS analysis, the tar samples were dissolved at a concentration of 1 mg per mL of THF. Different matrix chemicals were tested, but in the end, it was determined that the best results were obtained without using a matrix. The CTP samples were mounted in EpoFix resin and then polished prior to viewing under microscope to determine the mesophase content.

Results and Discussion

The FT-IR was used primarily to gain more information about the oxygen functional groups (1800-1650, 1300-1000 cm⁻¹) present in the tar samples. These regions were deconvoluted using OriginPro software, based on peaks previously defined by Ibarra and Painter^{4,5}. Table 1 shows the integrated results for these regions and they indicate that as secondary pyrolysis residence times increase, the concentrations of oxygen functional groups decrease (carboxylic/carbonyl, and phenolic/ether). The values shown in Table 1 were calculated by similar equations to the semi-quantitative relationships reported by Xueqiu et al⁶.

Table 1. The integrated FT-IR regions for oxygen groups

	U-CT-0	U-CT-1	U-CT-1.4	U-CT-1.8	U-CT-18	CTP-A	CTP-B
F_{carb}	0.410	0.495	0.118	0.215	0.168	0.056	0.478
F_{phen_eth}	2.610	2.003	1.405	0.961	1.087	0.817	2.133
F_{total oxy}	3.020	2.499	1.523	1.177	1.255	0.873	2.611

The integrated NMR results are shown in Table 2 below, and they show that as gas phase residence times increase, the aromatic and aliphatic content increase and decrease, respectively. The hydrogen donor concentrations were determined by integrating the 4.5-3.0 ppm region, which includes fluorene and acenaphthene-type groups as determined by the HSQC experiments. The hydrogen donor groups also appeared to be decreasing with increasing residence time.

Table 2. Integrated ¹H NMR regions

	F _{aromatic}	F _{aliphatic}	F _{alpha}	F _{beta}	F _{gamma}	F _{H donor}
U-CT-0	0.173	0.827	0.222	0.370	0.104	0.025
U-CT-1	0.392	0.608	0.321	0.133	0.030	0.073
U-CT-1.4	0.635	0.365	0.223	0.028	0.004	0.059
U-CT-1.8	0.735	0.265	0.179	0.008	-0.001	0.045
U-CT-18	0.757	0.243	0.167	0.015	0.001	0.037
CTP-A	0.869	0.131	0.072	0.008	0.001	0.043
CTP-B	0.493	0.507	0.220	0.141	0.050	0.042

The molecular weight (MW) distributions of the samples were obtained using MALDI-MS and the number-averaged and weight-averaged MWs are shown in Table 3. The average MWs indicate that as the residence time increases from zero to one second, there is initial cracking that occurs,

resulting in lower MW, but as time increases from one to 18 seconds, condensation reactions result in higher MW species. Closer observation of the MW distributions (not shown) for U-CT-1.4, 1.8, 18, and CTP-A show increasingly similar distributions of U-CT samples towards CTP-A.

Figure 1 shows polarized microscopy images of the CTP samples after three hours of heat soaking at 425 C. The results show that the samples with the longest pyrolysis residence times have the best mesophase coalescence. The results here support what is previously reported in the literature that higher concentrations of oxygen and aliphatic groups yield poorer bulk mesophase formation^{7,8}.

Table 3. Average MW of tar samples

Sample	M _N (g/mol)	M _w (g/mol)
U-CT-0	313	325
U-CT-1	301	314
U-CT-1.4	308	328
U-CT-1.8	322	349
U-CT-18	337	368
CTP-A	368	411
CTP-B	335	353

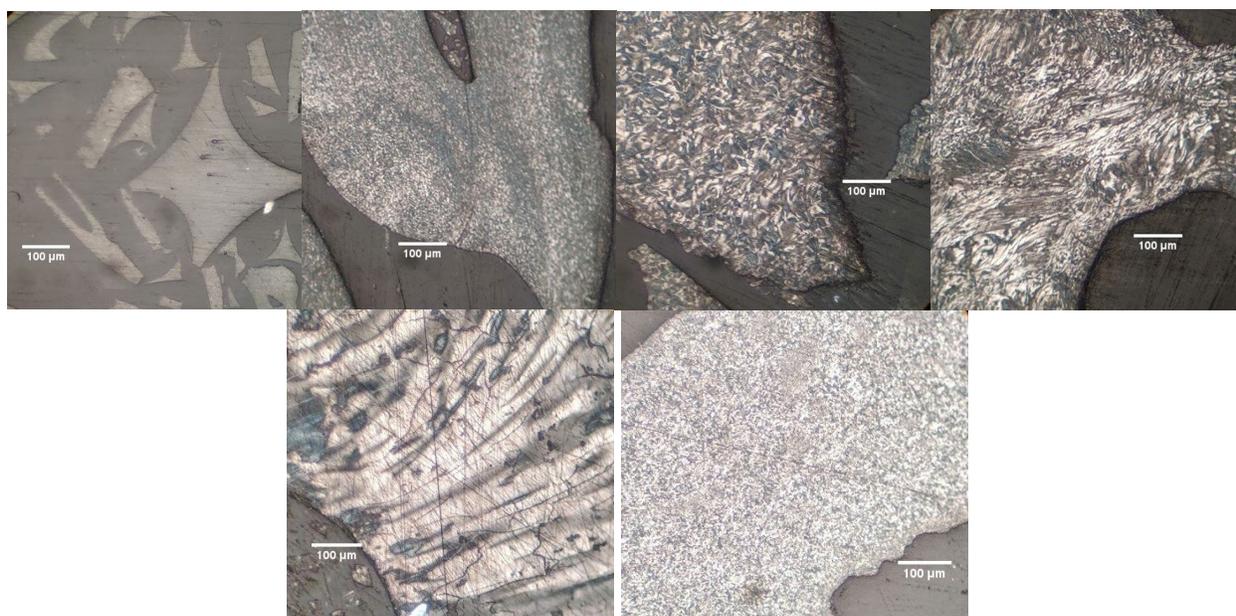


Figure 1. Microscope images of U-MCTP-0, 1.4, 1.8, 18, MCTP-A, MCTP-B (from left to right)

Conclusions

It is shown here that even a coal which is initially a poor choice for mesophase production, can be improved significantly by simply increasing secondary pyrolysis gas-phase residence times. From the FTIR and NMR results, it can be inferred that most of the gas-phase cracking occurs in secondary pyrolysis residence times of around two seconds at the conditions investigated. MALDI-MS data shows that beyond residence times of two seconds condensation reactions likely dominate, which lead to larger PAHs and are better for mesophase formation. In all analyses performed, coal tar samples with increasing residence times approach the results given by CTP-A, which is an excellent precursor to high modulus CF production. CTP-B has a similar oxygen and aliphatic content to U-CT-1 and 1.4 and does not perform well for creating mesophase. The approach of using pyrolysis secondary reactions should work on other coals that are not ideal for mesophase pitch production, and will be a focus of future work in this group.

Acknowledgments

The authors gratefully acknowledge funding to support this work from the Department of Commerce Economic Development Administration - Project No. 05-79-05831, the State of Utah - Governor's Office of Energy Development, the University of Utah Research Foundation, the University of Kentucky Research Foundation, and the Utah Advanced Materials & Manufacturing Initiative.

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