

SUBTASK 5.2 – DEVELOPMENT OF CARBON PRODUCTS FROM LOW-RANK COALS

Final Report

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SUBTASK 5.2 – DEVELOPMENT OF CARBON PRODUCTS FROM LOW-RANK COALS

EXECUTIVE SUMMARY

The goal of this project is to facilitate the production of carbon fibers from low-rank coal (LRC) tars. To this end, the effect of demineralization on the tar yields and composition was investigated using high-sodium and high-calcium lignites commonly mined in North Dakota. These coals were demineralized by ion exchange with ammonium acetate and by cation dissolution with nitric acid. Two types of thermal processing were investigated for obtaining suitable precursors for pitch and fiber production. Initially, tars were produced by simple pyrolysis of the set of samples at 650°C. Since these experiments produced little usable material from any of the samples, the coals were heated at moderate temperatures (380° and 400°C) in tetralin solvent to form and extract the plastic material (metaplast) that forms at these temperatures.

In the initial experiments, the six samples were pyrolyzed under nitrogen and tar at 650°C, and fixed carbon yields were determined. In addition, the tars were analyzed by gas chromatography (GC) to determine the yields of volatile soluble tars (VST) and their composition. The results showed only a small improvement in the yields of total tars as a result of demineralization of the high-sodium lignite. However, the yields of VST as determined by GC actually decreased for the ion-exchanged coal. Both total tars and VST were low for the high-calcium lignite and demineralized sample. The composition of the VST obtained from the six samples did not vary much. Thus the null hypothesis that the volatile organic tars produced from demineralized coals have the same composition as those from the raw coals has not been rejected. At this point, it appears that demineralization of the coals would not be useful in producing better and larger amounts of tars via pyrolysis. This is not a big issue, however, since plenty of tars are currently available from gasification of untreated lignite. What then remains is to demonstrate improved conversions of these tars or polar organics to pitches valuable for carbon fiber production.

In later experiments, much larger yields of tarlike metaplast extracts were produced during heating of the set of coals in tetralin at 380° and 400°C. The metaplast and tetralin are removed from unconverted coal, and then the highly aliphatic waxy material was removed from the extracts along with the tetralin solvent by dissolving the crude product in hexane. Thus the hexane-insoluble portion represents the most usable material for conversion to pitches and subsequently to fibers. In these experiments, the yields of hexane-insoluble metaplast showed a significant increase as a result of demineralization of both the high- and low-sodium coals. Not only are large amounts available via this processing, but this material is higher-melting than the tar fractions obtained earlier and, therefore, represents a more feasible approach to formation of the LRC pitch needed for the success of this project. Extraction at 400°C gave a much larger yield of the tetrahydrofuran-soluble, hexane-insoluble metaplast from the nitric acid-demineralized coal.

Conversion of the metaplast precursor to pitch was investigated by thermal and chemical cross-linking. Reacting the metaplast or a metaplast–tar mixture with methylal and acid catalyst produced a higher-melting cross-linked (but isotropic) product that could be drawn into a fine thread. These fibers were

stabilized by a programmed heating in air in a GC oven at 2?/min. These experiments demonstrated the potential for the use of LRC materials for isotropic pitches and fibers that can be activated and converted to general-purpose carbon fibers.

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INTRODUCTION

The conversion of coal tars to carbon fibers is of great interest, owing to the potential usefulness and commercial value of these products. The reported tar yields from low-rank coals (LRCs) have been substantially lower than the yields from higher-rank coals, typically 0.3 to 1 wt%. Several authors have described the effects of the dispersed cations in the LRC on pyrolysis yields and combustion rates. When cations were removed from the LRC, a substantial increase in the weight loss occurred during pyrolysis (1–4). Accordingly, the amount of tars condensed from the volatile stream in LRC pyrolysis was raised an order of magnitude by removal of coal cations. Not only do the organically bound cations retard the decarboxylation of the carboxylate groups of the coal, but the cations catalyze condensation (char-forming) reactions of the primary pyrolysis products before they can escape into the vapor stream.

Thus, if coal washing or exchange is employed prior to pyrolysis, the yields of tars generated could be increased to amounts feasible for commercial development. Some differences in the nature of the tar product from exchanged coals were noted, however (1). It is important to determine the impact of the dispersed cations on the useful characteristics of tars resulting from LRC pyrolysis. The economic value of the tars is determined by their potential for forming fibers, composites, and other anisotropic materials. High-strength anisotropic fibers are produced by melt-spinning, oxidizing, and carbonizing an anisotropic mesophase pitch formed by heating suitable tars at about 400°C. However, not all pitches can be spun to fibers. Pitches containing aromatics with substantial side chain substitution decompose before their viscosity is low enough to flow through the spinneret, and others may not form a mesophase without extensive sintering. Because LRC tars are likely to form side chain-substituted aromatic pitches and because of the expense of producing the mesophase pitch, an alternative process has been utilized for preparing useful fibers. A general-purpose carbon fiber (GPCF) is prepared by spinning an isotropic pitch instead of a mesophase pitch and carbonizing the fiber. The resulting isotropic carbons are low-strength, but may make excellent absorbents after steam activation. These products have very high surface areas, and the short fibers have excellent mass transfer properties.

OBJECTIVES

1. Determine the impact of organically associated (ion-exchangeable) cations as well as other cations on the quantity and composition of tars from a set of high-sodium and high-calcium lignites in pyrolysis experiments.
2. Determine the impact of organically associated (ion-exchangeable) cations as well as other cations on the quantity and composition of metaplast extracted at high temperatures from a set of high-sodium and high-calcium lignites.

- 3 Determine the effect of extraction temperature on the metaplast yield from as-received and demineralized lignites.
4. Determine the properties of the tar and metaplast products with respect to formation of pitches and fiber-forming potential.

RESULTS AND DISCUSSION

Task 1 – Production of Demineralized Coals

Two fresh North Dakota lignites (a high-sodium and a high-calcium) were ground, sized, and ion-exchanged by standard procedures using ammonium acetate to remove exchangeable cations. A second set of demineralized samples was prepared from the same coals using nitric acid to decompose carbonates and other salts. The two original and four treated samples were used in subsequent pyrolysis experiments.

Task 2 – Production of Coal Tars

During pyrolytic devolatilization of coals, aromatic and aliphatic semivolatile organic compounds are released into the gas flow and can be collected as a tar and subsequently heated to cross-link to a pitch. The goal is to maximize the amount of semivolatile tar by exchanging metal cations out of the LRC.

Exchanged and raw coals were pyrolyzed under nitrogen flow at 650°C, and tars were collected in a cold trap. The traps were extracted with dichloromethane to remove the organic- soluble fraction, leaving the aqueous fraction containing phenolics. The dichloromethane fraction was analyzed by GC to determine yields of VST or gas chromatographicable tars and their composition. The yield data for the set of lignite samples are reported in Table 1.

TABLE 1

Pyrolysis Yields from Lignite Set				
Coal	Carbon, %	Tar, %	VST, %	Gas ¹ , %
High-Na	(59.0)	(13.2)	0.87	(27.8)
Am. Ac.–High-Na	(57.02)	(14.24)	0.54	(28.74)
HNO ₃ –High-Na	(59.31)	(16.60)	0.85	(24.09)
High–Ca	(66.96)	(10.36)	0.37	(22.68)
Am. Ac.–High-Ca	(65.83)	(10.86)	0.43	(23.31)
HNO ₃ –High-Ca	(68.76)	(9.48)	0.56	(21.76)

¹ Weight of gas calculated by difference.

The ammonium acetate-exchanged product from high-sodium lignite showed a small decrease in fixed carbon and corresponding small increases in tar and gas yields. However, the VST fraction was substantially decreased. So it is likely that the yield of phenolics and other small polar organics was increased. Thus the removal of exchangeable sodium results in a few more volatiles, but they do not appear to be the kind needed for pitch formation. The tar yields are still very small.

The nitric acid-washed high-sodium lignite showed similar fixed carbon, somewhat more tar yield, and about the same amount of VST compared to the original coal. Thus it appears that the sodium has some ability to react with highly polar organics or at least inhibit their production.

The high-calcium lignite, both exchanged and unexchanged, showed less volatilization than the high-sodium lignite. The fixed-carbon yields were substantially higher, and both tar and gas yields were substantially lower compared to the high-sodium lignites. The VST yields are also substantially lower in the calcium coals. This appears to mean that the calcium is not effective in catalyzing volatilization of the coal at these temperatures, and its removal will not affect the yields much.

The composition of the tars (VST) as determined by GC analysis showed very little difference between the various coals. Especially important is that the ratios of methylated aromatics to unmethylated aromatics is not substantially different for the various tars. It is possible that some differences can be found in the phenolic content, but these have not been examined yet. Nevertheless, the null hypothesis that the volatile organic tars produced from demineralized coals have the same composition as those from the raw coals has not been rejected.

The hypothesis that exchange of the metal ions will result in substantially higher tar yields was rejected, especially with regard to the useful VST fraction. The amounts of VSTs were always less than 1 wt%. Thus the only feasible commercialization would utilize tars generated as by-products during coal gasification for making pitches. At the Dakota Gasification Plant large amounts of high-sodium lignites are gasified, so the low percent yields of tars are a significant factor.

The melting points of the hexane-insoluble tars were very low (<100°C). Heating under vacuum or in an airstream was not successful in reaching the desired melting temperature of about 225°C. The difficulty in converting these materials to a pitch may be due to the preponderance of alkyl aromatics in the products. Chemical cross-linking with electrophilic reagents may provide a better method for generating fiber precursors.

Task 3 – Production of LRC Metaplast Extracts

During pyrolytic devolatilization of coals performed as described above, aromatic and aliphatic semivolatile organic compounds were released into the gas flow and were collected as a tar that would be subsequently heated to drive off volatiles and cross-link to a pitch. This work established that exchanging metal cations out of the LRC did not significantly increase the yields of usable tar fractions.

An alternative approach to precursors for the LRC pitch was explored. This method obtains the metaplast, the plastic or tarlike material formed when coal is heated to temperatures of 350–400°C. At these temperatures, many of the carbon–oxygen bonds are broken, along with some carbon-carbon bonds, especially decarboxylation. These processes liberate water, phenolics, alcohols, CO₂, and other small polar species, and result in the formation of a plastic macromolecular gel (metaplast) from the remaining organics. Cations would be expected to stabilize the carboxylate groups and inhibit decarboxylation, resulting in less formation of metaplast or less soluble metaplast at lower temperatures. At higher temperatures, decarboxylation will occur, but more retrograde polymerization reactions are expected. Although previously demonstrated to give increased yields of soluble coal materials, no hydrogen, catalyst, or H₂S are added, since these increase the costs of the process enormously. Tetralin is added to dissolve the metaplast as it is formed and may help to stabilize or react with any free radicals remaining in the metaplast, which would subsequently result in retrograde polymerization to insoluble materials.

To determine the effects of cations of the metaplast extraction, exchanged and raw coals were heated in an autoclave under nitrogen pressure at 380°C. This is in the middle of the range for metaplast formation, and we might expect to observe greater effects for the metal ions. The product slurries were extracted with dichloromethane to remove the organic-soluble fraction and the tetralin, leaving the unreacted coal and moisture. The residue was dried and weighed (reported in Table 2 as CH₂Cl₂-insolubles). The conversion is the difference (in %) between this value and the initial dry

TABLE 2

Metaplast Extract (tetralin) Yields from the Lignite Set at 380°C
(coal = 15 g; tetralin = 30 mL; time = 1 hr)

Coal (Freedom mine)	CH ₂ Cl ₂ Insolubles, g	Conv. to CH ₂ Cl ₂ Solubles	Hexane Insolubles, g, mp (? C)	Conv. to Hexane Insolubles
High-Na	7.3	51	0.9 (135–147)	6
Am. Ac.–High-Na	10.8	28	1.5 (75–83)	10
HNO ₃ –High-Na	10.8	28	1.2 (90–115)	8
High-Ca	9.2	39	0.9 (78–81)	6
Am. Ac.–High-Ca	10.9	27	1.3 (95–110)	8.7
HNO ₃ –High-Ca	10.9	27	1.6 (60–75)	10.7

weight. The dichloromethane fraction was diluted with hexane to precipitate the more aromatic hexane-insoluble fraction (reported in Table 2). The tetralin and hexane-soluble aliphatics (waxes) are retained in the hexane. The usable metaplast yield data for the set of lignite samples are reported in Table 2 as percent conversion to hexane-insolubles. The melting points of the hexane insolubles are also reported in Table 2. The hexane solubles were analyzed by GC to determine yields of wax components and tetralin and naphthalene resulting from tetralin dehydrogenation.

Compared with the tar yields from pyrolysis experiments described above, the yields of metaplast extract were substantially higher. Furthermore, the yields of hexane-insoluble metaplast extract from the demineralized coals (8% to 10.7%) were much improved over those from the raw coals (6%). The high-sodium and the high-calcium lignites showed similar results for hexane-insoluble yields for both raw and demineralized coals. These results are consistent with the negative effect of cations expected for slower decarboxylation rates that would result in less metaplast or less soluble metaplast forming in the raw coals. The hypothesis that exchange of metal ions will result in substantially higher metaplast yields was not rejected.

On the other hand, the yields of dichloromethane solubles appeared to be higher for the raw coals compared with the exchanged coals. Therefore, there are other factors that need to be evaluated. An explanation for the difference in CH_2Cl_2 solubilities is that the CH_2Cl_2 is not extracting all the metaplast formed. Verification of this theory was attempted by further extracting the CH_2Cl_2 -soluble product with tetrahydrofuran (THF). For the CH_2Cl_2 insolubles from as-received coal, only 0.2 g was further extracted by the THF, whereas 0.9 g was extracted from the CH_2Cl_2 insolubles from the nitric acid-exchanged coal. This would correspond to 53% and 34% conversions to THF solubles, respectively, for the two coals. However, based on previous experience, it is likely that the metaplast remaining in a coal returns to a gel state on exposure to air and aging and becomes less soluble. Thus these conversions to THF solubles are not reliable for the reextracted samples. Better results were provided by the results described below where THF solubilities were determined initially in the higher-temperature runs.

Thermal extractions performed at higher temperatures ($>400^\circ\text{C}$) offer potential for increased metaplast yields. The null hypothesis to be rejected was that demineralized coals will generate higher yields of metaplast extract at higher temperatures. The as-received and demineralized coals were heated and extracted at a higher temperature, 400°C . The results for the as-received and nitric acid-demineralized coals are shown in Table 3. In these experiments, the solubility of the products was determined using three solvents (THF, CH_2Cl_2 , and hexane) instead of only the latter two. The higher-temperature reactions resulted in somewhat larger conversions to soluble materials. For the high-sodium coal, the conversion to THF solubles at 400°C was 63% (as-received basis). Most of the THF solubles were also soluble in CH_2Cl_2 ; thus the conversion to CH_2Cl_2 solubles was 61%, which can be compared with 51% at 380°C .

For the nitric acid-demineralized coal, the conversion to THF solubles was 67% at 400°C . However, a larger portion of the THF-soluble fraction was insoluble in CH_2Cl_2 . Thus the conversion to CH_2Cl_2 solubles was only 45%, compared to 28% at 380°C . Both samples, thus, exhibit improved conversions to soluble materials at the higher temperature. The main difference is that the material

TABLE 3

Metaplast Extract (tetralin) Yields from the Lignite Set at 400°C
(coal = 15 g; tetralin = 30 mL; time = 1 hr)

Coal (Freedom mine)	THF Solubles, %	CH ₂ Cl ₂ Solubles, %	Hexane Insolubles, g, mp (°C)	Conversion to THF Soluble, Hexane Insoluble, %
High-Na	63	61	2.8 (135–148)	20
HNO ₃ -exchanged High-Na	67	45	3.7 (45–50)	46

from extraction of the demineralized coal is less soluble in CH₂Cl₂. Unfortunately, the THF solubilities were not measured in the 380°C experiments; thus the lower CH₂Cl₂ conversions observed in the lower-temperature experiments are presumed to result from this lower solubility in CH₂Cl₂.

More importantly, however, the yield of THF soluble, hexane-insoluble extract was shown to increase dramatically for the nitric acid-demineralized coal. For the as-received coal, the hexane insolubles yield was 6% at 380°C and 20% at 400°C. For the nitric acid-treated coal, the hexane insolubles were 8% at 380°C but increased to 46% in the higher-temperature experiment at 400°C. The hexane-insoluble metaplast fraction is the polymeric (plastic) material that can be used to make the pitches for carbon fiber formation. Thus the substantial increase in amount of this material formed at the higher temperature is of great interest. The hexane-soluble material is much smaller molecular weight and more volatile; thus it cannot be cross-linked and converted to a pitch easily.

The hypothesis that demineralization will result in higher extraction yields at higher temperatures was not rejected, but the difference in THF solubles was not that great. The main difference that occurs in extraction of demineralized coals is that more hexane insolubles are generated. It seems likely that the sodium present in the high-sodium coal is affecting the thermal breakdown in coal structures, especially those that result in forming the smaller, more soluble materials.

The properties of the metaplast fractions obtained at both 380°C and 400°C were investigated. The melting points of the set of metaplast extracts show some variance, but with little discernable trend or explanation. In any case, they are consistent with high-molecular-weight coal macromolecules and are appropriate starting materials for conversion to higher-melting pitches. Generally, fibers are drawn at 220°C–250°C, so the extracts were heated in a vacuum and in air to drive off further volatiles and cross-link chains until the desired pitch is obtained.

The melting points of the hexane-insoluble product fractions from the set of coals extracted at 380°C are given in Table 2. These materials were heated in air to increase the melting points, but as with the tars, this was difficult. The CH₂Cl₂ insolubles did not, of course, melt but carbonized instead. The melting points of the THF solubles were above 250°C.

The hexane-insoluble, CH₂Cl₂-soluble fraction obtained from extraction of the as-received high-sodium lignite at 400°C had a melting point of 135–148°C (Table 3). Heating this fraction increased the melting temperature and gave a soft material that could be drawn to form very brittle fibers. The small amount of THF solubles obtained in the experiment melted over 250°C.

The melting point of the hexane-insoluble, dichloromethane-soluble fraction from the 400°C extraction of nitric acid-demineralized coal was very low (45–50°C), and after heating in air, the melting temperature did not increase to the temperatures required for drawing the pitch. The melting point of the dichloromethane-insoluble, THF soluble fraction was greater than 250°C. The melting point of the mixture of the two fractions was 150–160°C, thus the mixture of THF solubles with CH₂Cl₂ solubles was used as the precursor for formation of the pitch. This mixture was heated to increase the melting temperature and drawn at temperatures above 200°C to form fibers.

Task 4 – Preparation of Carbon Pitches and Fibers

Preliminary work in the formation of pitches and fibers from the metaplast extracts is described above. It should be stated that these extractions are much more expensive to carry out than simple pyrolysis technologies. Not only would demineralization have to be performed, but the large autoclaves for solvent extraction and distillation of solvents would increase the production cost by a large factor. Thus, in order to rapidly commercialize a technology for preparation of fibers from lignites, some way to prepare pitches from the tars currently available from lignite gasification is required. Some experiments were performed to evaluate the chemical cross-linking of these gasification tars. The gasification tars had been previously separated from the aqueous-soluble portions (phenolics) and the light components, such as BTEX (benzene, toluene, ethylbenzene, and xylenes), distilled off. This dry tar was a very viscous low-melting liquid.

The dry gasification tar as well as 1:1 mixtures with the metaplast extracts described above were chemically cross-linked by heating with methylal (20%) and 2% p-toluenesulfonic acid (PTSA) in chloroform solution. After stirring overnight, the solvent was removed by distillation, and the residue was further heated under a vacuum to remove volatiles. The product was air-blown at 100 to 150°C for 8 hr to increase the melting point and form the pitch.

In other experiments, a mixture of the metaplast extract was heated with phenol and formaldehyde in aqueous solution with the PTSA catalyst. The product was worked up similarly.

For the production of fibers, the pitches obtained as described above were drawn into fibers by pulling out the pitch slowly from the heated mass. The pitches from the cross-linked dry tar and from the

metaplast–phenol–formaldehyde mixture did not form fibers well above 150°C; that is, the melting points of the fibers were too low. Thus further curing of the pitch is needed for these materials.

In contrast, the pitches from crosslinking the 1:1 mixture of dry tar and metaplast were much harder, and could be easily rolled into beads without wetting the glass. The pitch was drawn at 150°C by slowly pulling a fiber with a glass rod. This procedure gave a thin fiber that dried instantaneously to a stable, nonsticking fine thread. The fibers were cured by heating in a GC oven using the following temperature program: initial temperature = 50°C (2 min); rate = 2 °/min to final temperature = 250°C; isothermal 5 min. The fibers exhibit some brittleness, but this is expected from the isotropic pitch precursor.

In conclusion, the methylal cross-linking cross-links the dry tar by itself and in mixtures, but further work is needed to determine the optimum curing temperatures. Although promising fibers were produced, the conditions used here were clearly inadequate for the preparation of high-melting- temperature pitches, especially from the dry tar alone. Other cross-linking agents should also be investigated for these materials. No work was performed with spinning fibers, so this also needs to be investigated. Finally, carbonization of the fibers to GPCFs and testing of their adsorption properties need to be performed.

CONCLUSIONS

The goal of this project was to facilitate the production of carbon fibers from LRC tars. The effect of demineralization on the tar yields and composition was investigated using the pyrolysis of high-sodium and high-calcium lignites and their ion-exchanged counterparts at 650°C. However, yields of volatile soluble tar products were very small, and little effect of demineralization on the yield was noted. The tars were not appropriate pitch precursors.

In contrast, conversion to the metaplast state by heating at 380–400°C in a tetralin phase gave much larger amounts of higher-molecular-weight precursors for pitch formation. THF effectively removed the metaplast from the coal matrix. Highly aliphatic, waxy material was removed from the extracts along with the tetralin solvent by dissolving the crude product in hexane. Thus the hexane-insoluble portion represents the most usable material for conversion to pitches and subsequently to fibers. In these experiments, the yields of hexane-insoluble metaplast showed a significant increase as a result of demineralization of both the high-sodium and low-sodium coals. Not only are large amounts available via this processing, but this material is higher-melting than the tar fractions obtained earlier and, therefore, represents a more feasible approach to formation of the LRC pitch needed for success of this project. Preliminary pitch and fiber-forming experiments showed promise for the metaplast material derived from demineralized lignite. Chemical cross-linking of gasification tars and metaplasts from lignites will generate a precursor suitable for a fiber-forming pitch.

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