

ANTHRACITES AS FEEDSTOCKS FOR BINDER PITCHES OR CARBON FIBERS

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Introduction

Low-temperature hydrogenation of anthracite to produce a liquid product that could have potential applications in carbon materials technology, such as binder pitches or precursors to carbon fibers, was investigated. Different anthracites were reacted with hydrogen donors and catalysts at 300°C using 1000 psi hydrogen gas in a microautoclave reactor. The rate of hydro-treating of the anthracite was correlated with an increased solubility in tetrahydrofuran (THF) of the resultant product. The results indicate that low-temperature hydrogenation of anthracite is possible. The yields and compositions of reaction products were compared with existing commercial materials to determine future applications of these anthracite-derived substances in manufacture of premium carbon products.

Due to its highly aromatic nature, low oxygen and other hetero-atom content and the possibility to achieve low ash levels, anthracite has been identified as an alternative feed-stock for the development of untraditional pitches. The key to successful use of anthracite for high-performance binder pitches may be the milling of the anthracite precursor to ultra-fine particles or powders, followed by tailored hydrogenation. Previous work has suggested that hydrogenation of anthracite is feasible [1,2]. Accordingly, this work deals with the progress in anthracite hydrogenation, with the goal of producing an aromatic pitch from hydrogenated anthracite.

Experimental

The elemental and proximate analyses of the anthracites used, LCNN and Buck Mountain, are listed in Table 1. The letters 'L' and 'B' denote the coal used in that run, where 'L' represents $\approx 250\mu\text{m}$ (-60 mesh) LCNN anthracite and 'B' represents $\approx 250\mu\text{m}$ Buck Mountain anthracite. The hydrogen donors used were dihydroanthracene (97%, Aldrich), dihydrophenanthrene (94%, Aldrich) and phenanthrene (98%, Aldrich).

The anthracites and hydrogen donor mixtures were charged into stainless steel microautoclave reactors of nominal 20 ml capacity in 3g batches. The reactors were pressurized with 1000 psi nitrogen or hydrogen gas and leak tested. Hydrogenation was conducted by immersing

Table 1. Analyses of anthracites.

Proximate (as rec'd) and Ultimate (dry)	Buck Mountain	LCNN
% Moisture	4.51	3.3
% Ash	6.52	6.7
% Volatile	3.49	4.5
% Fixed Carbon	85.48	88.3
% Carbon	88.85	95.7
% Hydrogen	1.29	1.5
% Nitrogen	0.78	1.2
% Total Sulfur	0.49	0.5
% Oxygen (by diff.)	1.76	1.0

the reactors in a Techne FB-08 fluidised sandbath. The reactors were agitated at an average of 100 cycles/min to keep reactants well mixed. After reaction the reactors were quenched to room temperature by submersing them in water. Reaction products were Soxhlet-extracted with THF. The THF used was HPLC grade from J. T. Baker, and extraction was conducted for 24 hours.

All runs with LCNN were carried out at 1000 psi H₂ and at 300°C. The catalyst used was molybdenum hexacarbonyl (Mo(CO)₆). The conditions for the runs using Buck Mountain anthracite used a 75/25% ratio by weight of hydrogen donor to coal under nitrogen or hydrogen and the soaking times varied from 3 to 48 hours.

Results and Discussion

The THF solubility of the products can be used as a good indicator of the degree of hydrogenation of anthracites, and Table 2 lists the THF extraction values for the runs with the LCNN anthracite. These reactions used dihydroanthracene and dihydrophenanthrene as hydrogen donors and molybdenum hexacarbonyl (Mo(CO)₆) as a catalyst. Mo(CO)₆ was used because it has been reported as a good coal liquefaction catalyst [3, 4] and has a relatively low melting point, 150°C, suitable for this low-temperature reaction. Therefore, Table 2 also compares the use of different amounts of catalyst used in the reactions as well as different hydrogen donors. There is a difference of 3.9 % between using a coal to hydrogen donor ratio of 1 to 1 and a ratio of 1 to 2, as seen by comparing runs 2L and 3L. However, since there is not an increase in THF solubles with an increase in hydrogen

donor, it confirms that the THF-soluble product is not unreacted hydrogen donor, but that some coal reaction has occurred. Another comparison, between runs 2L and 4L, confirms that there is not a significant difference in THF-soluble yield between a 10 to 1 coal to catalyst ratio and a 2 to 1 ratio. Therefore, a 10 to 1 ratio was used throughout the remainder of the experiments where catalyst was added. Furthermore, dihydrophenanthrene seems to produce fewer THF solubles than dihydroanthracene, as shown by the comparison of run 2L and 7L.

Table 2. Comparison of THF-soluble yields for different H-donors and catalyst ratios.

	Hydrogen Donor	Coal/Cat	THF Sols.
2L	Dihydroanthracene	10 to 1	41.5 %
3L	Dihydroanthracene*	10 to 1	37.6 %
4L	Dihydroanthracene	2 to 1	42.7 %
5L	None	10 to 1	<1 %
7L	Dihydrophenanthrene	10 to 1	33.1 %

*Run 3L has a 1 to 2 ratio of coal to dihydroanthracene, whereas all other have 1 to 1 ratio.

Table 3 compares the use of different heating profiles on the Buck Mountain anthracite. The results of this comparison show that more reaction occurs when reacted longer and at higher temperatures. Table 4 compares reactions over a 48-hour period under different conditions for Buck Mountain anthracite. Run 11B had no catalyst and was under nitrogen gas, whereas run 12B had a 10 to 1 ratio by weight of coal to Mo(CO)₆ and was under hydrogen gas. The results are inconsistent with the results from experiments performed above. It was expected that with the catalyst and under hydrogen gas, more coal would break apart and produce liquid products.

Table 3. THF-soluble yields for Buck Mountain.

	Heating Profile	THF Solubles
9B	200°C for 3 h	8.4 %
10B	200°C for 3 hours; 6°C/min to 500°C; 2h hold at 500°C	30.1 %

Table 4. THF-soluble yields for Buck Mountain, 48 h.

	Catalyst and Gas Used	THF Solubles
11B	No catalyst under N ₂	58.9%
12B	Mo(CO) ₆ under H ₂	10.6%

Experimentation has been done to analyze the effect of coal particle size on hydrogenation reactions. The reactions in this set of data were performed on LCNN anthracite, dihydroanthracene as hydrogen donor, and molybdenum hexacarbonyl as the catalyst under 1000 psi hydrogen and reacted at 300°C. The reactant ratio reflects the amount of coal that is reacted with hydrogen donor and catalyst, respectively. Runs 17L and 18L

represent the control group, where no hydrogen donor or catalyst was used. Runs 19L and 20L represent a normal reaction using hydrogen donor and catalyst. This data is summarized briefly in Table 5.

Table 5. THF-solubles for different particle sizes.

	Reactant ratio*	Part. Size (μm)	THF Sols.
17L	10:0:0	250	0.0 %
18L	10:0:0	17	6.1 %
19L	10:10:1	250	41.5 %
20L	10:10:1	17	46.0 %

*Coal : hydrogen donor : catalyst.

A clear correlation can be made relating particle size to hydrogenation of anthracite. Coal having a particle size of ≈17μm produces more THF-solubles than coal having a particle size of ≈250μm. This data is promising, but does not take into account the possibility that the coal macerals may be distributed differently, or other unforeseen changes that may occur, when coal is ground to small particle sizes.

Conclusions

Dihydroanthracene works well as a hydrogen donor at a 1 to 1 ratio by weight of coal to hydrogen donor and Mo(CO)₆ works well as a catalyst at a 10 to 1 ratio by weight of coal to catalyst for producing a THF-soluble product from ≈250μm LCNN anthracite at low temperatures. There is evidence that reactions on ≈250μm Buck Mountain anthracite occur somewhere between 200°C and 500°C. Also, coal particle size has an effect on the production of THF-solubles produced where smaller particle size increases THF-solubles.

The results presented above support the hypothesis that anthracites can be reacted at low temperatures to produce a THF-soluble liquid product. This coal-derived liquid will, conceptually, consist of large aromatic molecules. Such a liquid, having these properties, has potential to have applications in carbon materials technology as, e.g., binder pitches or precursors to carbon fibers.

References

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