

Nanofuel/Oxidizers For Energetic Compositions

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ABSTRACT

The objective of this task was to prepare and characterize nano porous carbon with adsorbed liquid and solid oxidizers and explosives as a new energetic component for thermobaric explosive formulations. Based on the adsorption process determined through the use of the inert compounds butanetriol and naphthalene, the infusion of nitrate ester plasticizer butanetriol trinitrate (BTTN) and the explosive HMX into nano porous carbon was demonstrated. The sensitivity and thermal properties were also determined.

INTRODUCTION

Current thermobaric (TBX) formulations are limited in providing effective impulse over the full range of expected applications. A high impulse can be measured from detonating fuel rich formulations in a closed system or a confined space, but incomplete combustion results in tunnels where fuel rich compositions cannot fully utilize the energy from metal oxidation to support secondary combustion (Beiter 2003). For example, high graphite containing formulations perform well in bomb-proof measurements, but do not provide an efficient energy release in a tunnel test (Mychajlonka, 2003). Here a new energetic ingredient is prepared with oxidizers adsorbed into a high surface area nano porous carbon to replace graphite in fuel rich formulations. This route provides an intimate mixture of oxidizer with the fuel source, and will maintain thermobaric performance in both confined spaces and extended tunnels. In addition, nano scale intimate mixing of a fuel and oxidizer is expected to increase the combustion efficiencies and burning rates relative to macro scale mixing. This leads to a new energetic ingredient for applications in fast burning propellants, thermobaric formulations, perchlorate replacements, and new primers and pyrotechnics.

RESULTS AND DISCUSSION

Nano Porous Carbon

The pore size and pore structure of the activated carbon make a huge difference in how well materials are adsorbed. The pore size and pore structure depend upon the raw material and the activation process used to produce the activated carbon. Activated carbon is typically manufactured from peat, hard and soft wood, lignite coal, bituminous coal, coconut shell, olive pits and specialty

materials. Carbon is usually activated by steam or chemical treatment (Walker, Jr., 1966).

Steam activation involves two steps: carbonization and activation. Carbonization is carried out at elevated temperatures in an oxygen-lean environment to convert the raw material into a disordered carbon structure with a low volatile content. Steam activation is carried out at 1800°F. At this temperature carbon reacts with the steam to form carbon monoxide and hydrogen that exit as gases to create a highly porous carbon material. Chemical activation involves the use of acid in wood-based carbons to produce a very high pore volume.

Activated carbon is available in three forms or shapes: powder, granular and extruded. For explosive applications only powdered activated carbons will be used. Table 1 below shows three key properties of the various types of activated carbon.

Table 1. Key Properties of Various Types of Activated Carbon*

Carbon Type	Pore Volume (ml/g)	Mean Pore Radius (Angstroms)	Surface Area (m ² /gm)
Coconut Shell	0.5 - 0.6	10 - 11	1000 - 1100
Peat	0.6 - 0.7	11 - 12	1000 - 1275
Bituminous Coal	0.6 - 0.7	12 - 14	1000 - 1150
Bituminous Coal	0.7 - 0.8	14 - 16	900 - 1050
Lignite Coal	0.9 - 1.0	29 - 32	600 - 675
Peat	1.1 - 1.2	23 - 26	900 - 1050
Wood Acid Activated	1.4 - 1.8	22 - 26	1200 - 1600

* NORIT Americas Inc.

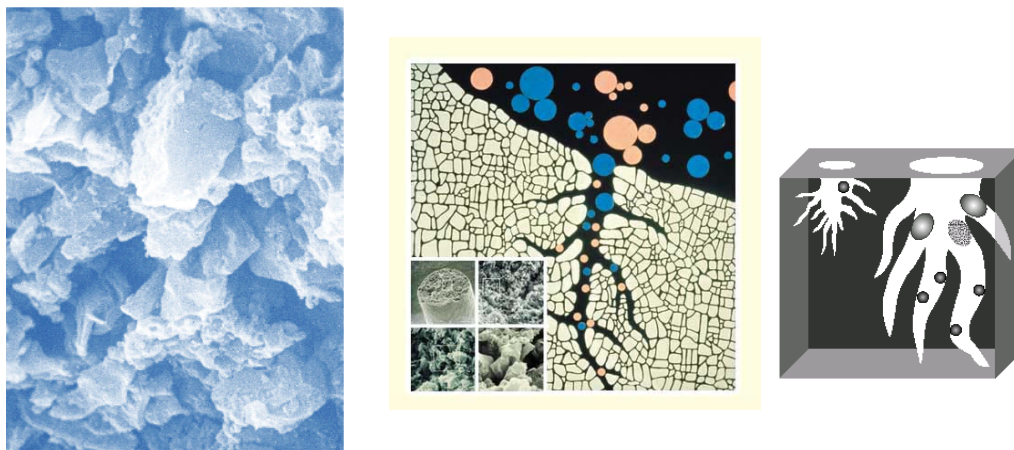
The activated carbon powder, Fisher Scientific Cat. No. C272-500, was used for performing this study, and the properties of this product are shown in Table 2.

Table 2. Properties of Fisher Scientific Nano Porous Carbon Powder.

Property	Value
Raw Material/Activation	Peat/Steam Activated
Particle Size	>150 microns
Internal Surface Area (BET)	90 m ² /gm
Apparent Density (Tamped)	350 kg/m ³
Ph	7 (Neutral)
Acid Soluble Matter	0.5% (max. 3 1/2%)
Moisture	8% (max. 10%)

Infusion Technology

Infusion of energetic materials into angstrom-sized pores is a new approach in nano scale mixing of fuel/oxidizer systems. This adsorption process can be amenable to any soluble oxidizer, and an intimate mixture of fuel/oxidizer at the molecular scale can be attained through the selection activated carbon with the appropriate pore size and surface area. A schematic of infusion into nano pores is shown in the figure below.



Infusion of Energetic Materials into Activated Carbon Nano Pores

Modeling Adsorption Behavior of Butanetriol, Naphthalene, BTTN and HMX

The adsorption energies can be calculated and the adsorption behavior can be modeled for the infusion of organic nitrate esters and explosives into the carbon substrate. To model adsorption behavior of butanetriol, naphthalene, BTTN, and HMX in activated carbon, the following configurations of these molecules on carbon were considered:

- Butanetriol – 4 C-carbon bonds, and 2 O-carbon bonds, 5 intersegmental bonds; other bonds are thermalized.
- Naphthalene – 10 C-carbon bonds, 4 intersegmental bonds.
- BTTN – 4 C-carbon bonds, 3 O-carbon bonds, and 3 N-carbon bonds, 5 intersegmental bonds; other bonds are considered thermalized.
- HMX – 4 C-carbon bonds, 2 O-carbon bonds, and 4 N-carbon bonds, 4 intersegmental bonds; other bonds are considered thermalized.

To estimate the adsorbate/adsorbate energy ε and adsorbate/adsorbent energy ε_S can be estimated from the carbon bonded, oxygen bonded, and nitrogen bonded segments of molecules. For a carbon-carbon bond, ε_S is known to be about 1.67 Kcal/mol (Aranovich, Donohue, 1999), which gives an $\varepsilon_S /kT \approx -2.8$ per each carbon bond at $T = 293$ K. Using the isosteric heat of adsorption for CO_2 on activated carbon, which is about 6 Kcal/mol, the ε_S for oxygen-carbon bonds can be calculated as shown (Valensuela, and Myers, 1989):

$$\varepsilon_S (\text{O-}) = \frac{1}{2} [\varepsilon_S (\text{CO}_2) - \varepsilon_S (\text{C-})] \approx \frac{1}{2} (6 - 1.67) \approx 2.2 \text{ Kcal/mol}$$

The ε_S for nitrogen-carbon bonds is approximately equal to that of carbon-carbon bonds.

Using these assumptions and putting each segment-segment van der Waals energy of interaction ≈ -0.2 (Aranovich, and Donohue, 1999) we obtain adsorbate-adsorbate energy ε and adsorbate-adsorbent energy ε_S for each compound listed in Table 3.

Table 3. Calculated Adsorbate-Adsorbate Energy ε & Adsorbate-Adsorbent Energy ε_S

Absorbate	Adsorbate/Adsorbate Energy	Adsorbate/Adsorbant Energy
butanetriol	$\varepsilon /kT \approx -1.0$	$\varepsilon_S /kT \approx -18.6$
naphthalene	$\varepsilon /kT \approx -0.8$	$\varepsilon_S /kT \approx -28.0$
BTTN	$\varepsilon /kT \approx -1.0$	$\varepsilon_S /kT \approx -22.3$
HMX	$\varepsilon /kT \approx -0.8$	$\varepsilon_S /kT \approx -29.8$

These energies were used for modeling adsorption behavior of butanetriol, naphthalene, BTTN, and HMX, in nano porous carbon.

Adsorption Modeling

Computer modeling of adsorption behavior for butanetriol, naphthalene, BTTN, and HMX in nano pores of activated carbon was performed using Density Functional Theory (DFT) (Aranovich and Donohue 1999). DFT allows calculations of density distributions in pores and adsorption isotherms with two variable parameters (1) energy of adsorbate-adsorbate interaction ε/kT and (2) energy of adsorbate-adsorbent interaction ε_S/kT . Figure 1 shows adsorption (a) as a function of reduced density (x) for BTTN in nano pores of activated carbon at $\varepsilon/kT = -1.0$ and $\varepsilon_S/kT = -22.3$. Figure 2 illustrates adsorption isotherms for HMX

in activated carbon at $\varepsilon/kT = -0.8$ and $\varepsilon_S/kT = -29.8$. As seen from Figures 1 and 2, for wider pores, adsorption saturation occurs at higher concentration of adsorbative. Also, same amounts of HMX can be loaded into pores of activated carbon at much lower concentrations in solution (compared to BTTN).

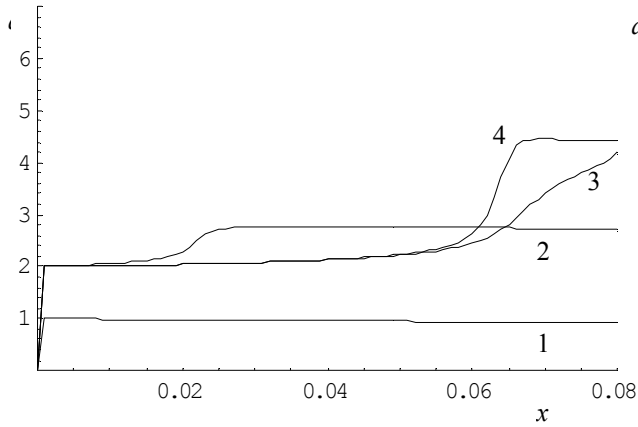


Figure 1. Adsorption isotherms for BTTN in slit-like nano-pores of activated carbon predicted by Density Functional Theory for various distances between walls (in molecular diameters): 1 (1), 3 (2), 5 (3), and 7 (4). Here $\varepsilon/kT = -1.0$, and $\varepsilon_S/kT = -22.3$.

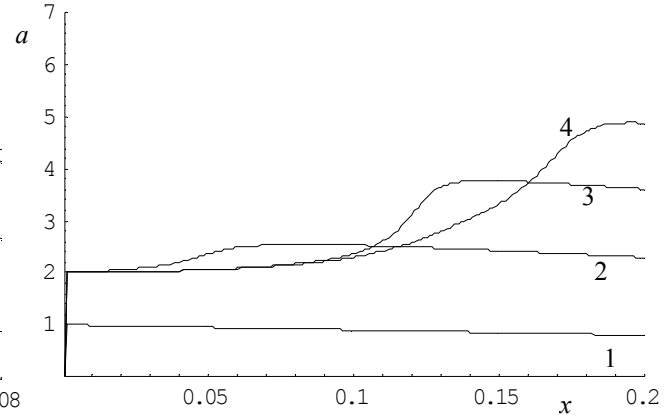


Figure 2. Adsorption isotherms for HMX in slit-like nano-pores of activated carbon predicted by Density Functional Theory for various distances between walls (in molecular diameters): 1 (1), 3 (2), 5 (3), and 7 (4). Here $\varepsilon/kT = -0.8$.

Figure 3 shows adsorption isotherms for butanetriol in nano pores of activated carbon at $\varepsilon/kT = -1.0$ and $\varepsilon_S/kT = -18.6$. A comparison of Figure 1 and Figure 3 shows that slight decrease of ε_S/kT (by 16 %) results in insignificant quantitative changes of adsorption isotherms, thus butanetriol can be used for experimental modeling of the adsorption behavior of BTTN in activated carbon. Figure 4 shows adsorption isotherms for naphthalene in nano-pores of activated carbon at $\varepsilon/kT = -0.8$ and $\varepsilon_S/kT = -28.0$. Comparison of Figure 2 and Figure 4 shows that, in this case also, slight decrease of ε_S/kT (by 6 %) results in insignificant quantitative changes of adsorption isotherms, and naphthalene can be used for experimental modeling of the adsorption behavior of BTTN in activated carbon.

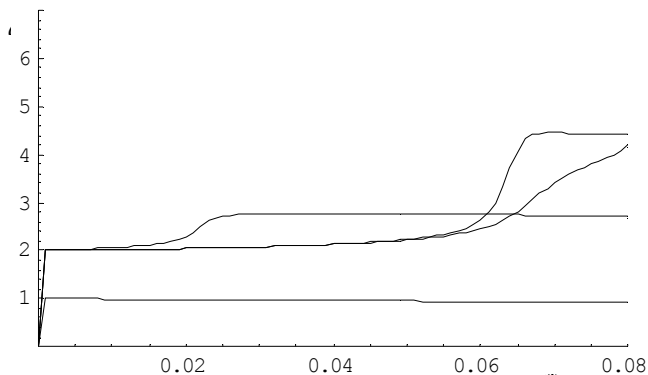


Figure 3. Adsorption isotherms for butanetriol in slit-like nano-pores of activated carbon predicted by Density Functional Theory for various distances between walls (in molecular diameters): 1 (1), 3 (2), 5 (3), and 7 (4). Here $\varepsilon/kT = -1.0$, and $\varepsilon_S/kT = -18.6$.

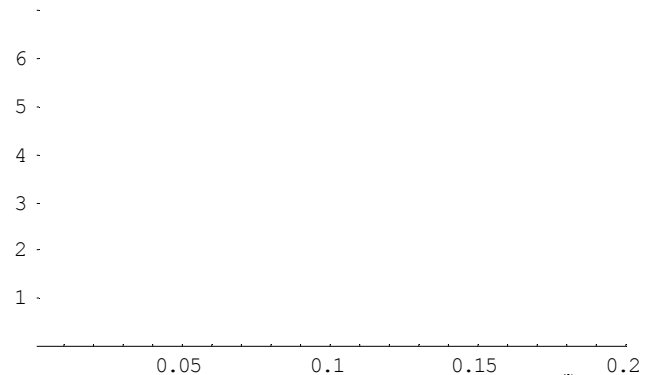


Figure 4. Adsorption isotherms for naphthalene in slit-like nano-pores of activated carbon predicted by Density Functional Theory for various distances between walls (in molecular diameters): 1 (1), 3 (2), 5 (3), and 7 (4). Here $\varepsilon/kT = -0.8$, and $\varepsilon_S/kT = -28.0$.

Butanetriol and Naphthalene Adsorption Procedure

Activated carbon (Lot #033560) was obtained from Fisher. Naphthalene (Lot #A017993301) and 1,2,4-butanetriol (Lot #A002386201) were obtained from Acros organics. All chemicals were used without further purification. Glassware and spatulas were cleaned by rinsing with acetone, ethanol, and finally soaking in water. In cases where large amounts of naphthalene were used, an intermediate step was added where the glassware was scrubbed in a solution of roughly 1% Alkonox (Alkonox, Inc.), followed by soaking and rinsing in water. All clean glassware was handled only while wearing gloves. This was done in order to prevent the addition of fingerprints to the beakers, which will show up on a sensitive electronic balance and can change the mass of the beaker in an uncontrolled manner.

Stock solutions of roughly 10% naphthalene, 20% naphthalene, 10% butanetriol and 20% butanetriol (all in acetone and all percentages by mass) were made in advance of the experiments and stored in sealed 100 mL glass jars at room temperature.

Evaporation experiments were performed in a fume hood with an electronic balance accurate to four decimal places. A clean, dry 50 mL beaker was first preweighed, and then filled with a known amount of activated carbon. Next, either acetone or a stock solution of naphthalene or butanetriol dissolved in acetone was added to the beaker. The total mass of carbon and solution was then allowed to evaporate while sitting on the balance. We opened the glass plate above the balance chamber to aid the evaporation process. The total mass of the carbon and solution was recorded at regular time intervals until it became roughly constant.

In order to determine the maximum loading of naphthalene in activated carbon, a known amount of carbon was first placed into a clean 50 mL beaker. Next, enough 20% stock solution was added to give the desired total loading. This solution was then diluted with additional acetone until all of the activated carbon was submerged. The beaker was allowed to sit uncovered in the fume hood overnight, and was visually inspected in the morning for residual naphthalene. A digital camera was used to capture images of the samples.

Maximum Loading Experiment

The maximum loading of material by adsorption into activated carbon was tested with a 24.77 % solution of naphthalene in acetone. Naphthalene was chosen because the non-adsorbed fraction will show up as a white, crystalline solid, which is easy to identify by inspection. Six trial runs were set up as described in the materials and methods section. These trials had naphthalene concentrations listed below in Table 4.

Table 4. Data for Maximum Loading of Nano porous Carbon with Naphthalene

Trial	Activated Carbon (g)	Naphthalene (g)	% Naphthalene by Mass
1	0.2810 g	0.1746 g	62.15 %
2	0.1835 g	0.1468 g	80.02 %
3	0.1652 g	0.1541 g	93.28 %
4	0.1800 g	0.1904 g	105.81 %
5	0.4031 g	0.4526 g	112.27 %
6	0.3195 g	0.3963 g	124.04 %

Results of modeling and experiments with butanetriol and naphthalene indicate that loading of BTTN and HMX in nano porous activated carbon can be performed from acetone solutions at a room temperature. It can be concluded that approximately 105 % - 112 % naphthalene by mass (1:1 weight ratio) can be loaded into activated carbon by the evaporation method.

Fuel/Oxidizer Compatibility Tests

The compatibility of the nitrate ester plasticizer BTTN and the explosive HMX was determined by performing Differential Scanning Calorimetry tests on the following samples:

1. Activated Carbon
2. BTTN
3. BTTN w/ 1% 2NDPA
4. BTTN w/ 1% 2NDPA Doped Activated Carbon
5. HMX Holston #87B240-021
6. HMX Holston #87B240-021 in Activated Carbon

The measurements were made on milligram samples of material under nitrogen in sealed aluminum pans using a heating rate of 5°C/minute. The DSC data is provided in Appendix A.

The DSC data for BTTN w/ 1% 2NDPA/activated carbon showed an approximately 8-9 °C negative shift in the peak temperature compared to that of BTTN w/ 1% 2NDPA. This shift indicated a “slight degree of incompatibility”.

The DSC data for HMX/activated carbon showed an approximately 43-49 °C negative shift in the peak temperature compared to that of HMX. This shift is indicative of a significant degree of incompatibility. This demonstrates the fact

that the choice of activated carbon type may be very influential in the stability of the nanofuel/oxidizer compositions. Different types of steam activated carbon are also available and can be tested to determine material would be more suitable for HMX adsorption.

Adsorbed Energetic Hand Mixes

Based on the above results of the inert adsorbent studies, a 1:1 weight ratio for the activated carbon/BTTN and the activated carbon/HMX fuel/oxidizer compositions were prepared at a 4 g scale for the purpose of obtaining compatibility and sensitivity data.

Activated Carbon/BTTN/2NDPA (No. IH230-03L-NANOC-0587)

Beginning with 2.0 g BTTN, butantriol trinitrate, in approximately 30 ml of acetone was added 2.0g of activated carbon while stirring. The mixture was stored in at ambient temperature in a fume hood overnight.

Activated Carbon/HMX (No. IH230-03L-NANOC-0588)

To 125 g acetone weighed into a plastic beaker was added 2.0 g of HMX. This was stirred until the HMX was completely resolved, approximately 5 minutes. 2.0 g of activated carbon was added to the HMX solution while stirring. This mixture was placed in a fume hood and the acetone was allowed to evaporate overnight.

Adsorbed Energetics Sensitivity Tests

Sensitivity testing consisting of the NOS Impact, ABL Friction and ABL ESD tests was performed on samples from the hand mixes described above. The data from the sensitivity tests is shown in Table 5 below.

Table 5. Sensitivity Testing for Activated Carbon*

SAMPLE ID MIX NO.	NOS IMPACT 50% hgt. (mm)	ABL FRICTION 20 TIL (psig)	ABL ESD 20 TIL (joules)
Act. Carbon/BTTN/2NDPA IH230-03L-NANOC-0587	108 (M)	135 (M)	0.165 (M)
Act. Carbon/HMX IH230-03L-NANOC-0588	57 (H)	100 (M)	0.165 (M)
RDX Standard	303 (M)	135 (M)	0.326 (M)

*Memo 5100 Ser 350DR/319/dr dated 9 December 2003

CONCLUSIONS & RECOMMENDATIONS

- Results of modeling and experiments with butanetriol and naphthalene indicate that loading of BTTN and HMX in nano-porous activated carbon can be performed from acetone solutions at a room temperature. It can be concluded that approximately 105 % - 112 % naphthalene by mass (1:1 weight ratio) can be loaded into activated carbon by the evaporation method.
- Hand mixes indicate that the BTTN can be successfully adsorbed in a 1:1 weight ratio. The activated carbon/BTTN/2NDPA compatibility and sensitivity results show adequate stability and sensitivity for optimization and scale-up.
- The initial hand mixes show that that it is feasible to adsorb the HMX using activated carbon but at less than a 1:1 weight ratio. The sensitivity tests results (showing high sensitivity) were most likely affected by the presence of unadsorbed HMX.
- The results of the hand mixes of activated carbon/HMX indicate that additional trials are needed to establish the proper type of activated carbon and the ratio of activated carbon to HMX to required obtain complete adsorption of the HMX.
- The activated carbon/BTTN/2NDPA formulation should be optimized to incorporate the maximum amount of BTTN possible into the Fisher Scientific activated carbon. The optimized formulation should be scaled up for evaluation in the HGS-4 explosive formulation. Additional stability tests such as the vacuum stability or the nitrogen Talliani should be performed to verify the stability of the activated carbon/BTTN/2NDPA formulation.

REFERENCES

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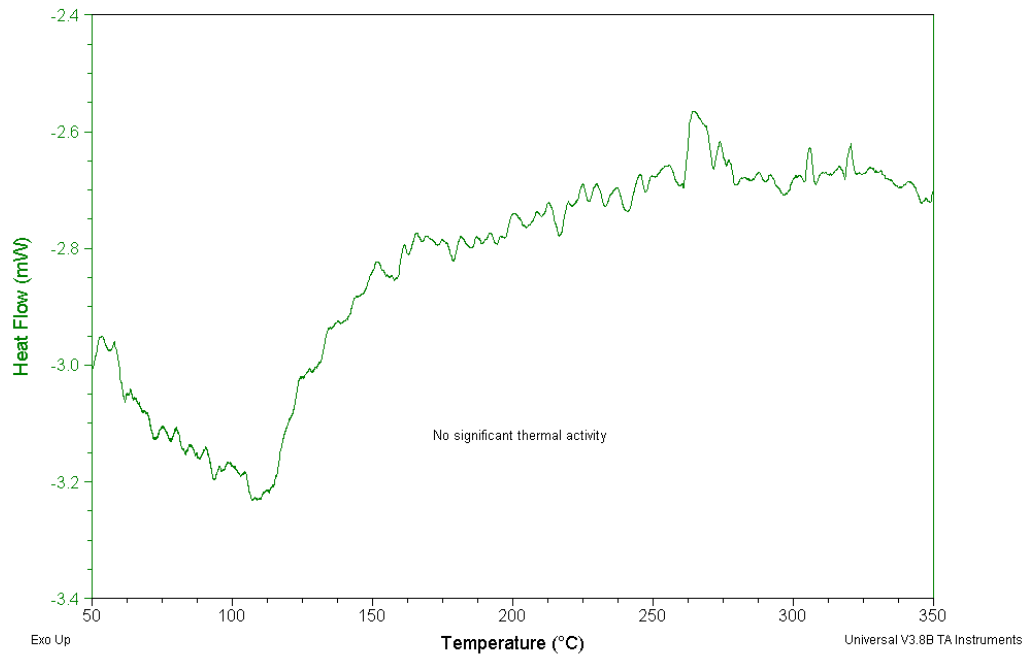
P. L. Walker, Jr. (1966), "Chemistry and Physics of Carbon," Marcel Dekker, Inc. New York page 51.

APPENDIX A.

Sample: ACTIVATED C @5°C/MIN
Size: 1.0800 mg
Method: 5°C/MIN FROM 35 TO 350°
Comment: N2,SEALED AL PANS,102903/418.49/157.75/0.8285/-16.69/0.4

DSC

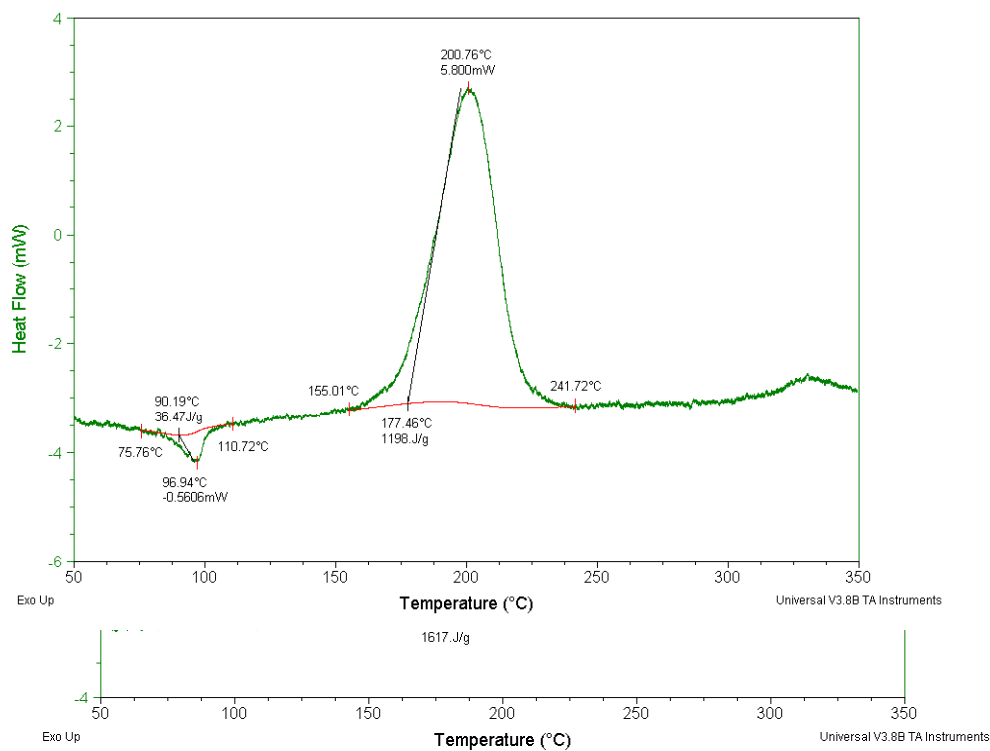
File: D:\TAD\data\910-950\D1actc.617
Operator: DNS/DLK 56.96/57.08
Run Date: 30-Oct-03 06:13



Sample: BTTN 1% 2NDPA @5°C/MIN
Size: 1.5800 mg
Method: 5°C/MIN FROM 50 TO 350°
Comment: N2,SEALED AL PANS,102903/418.49/157.75/0.8285/-16.69/0.4

DSC

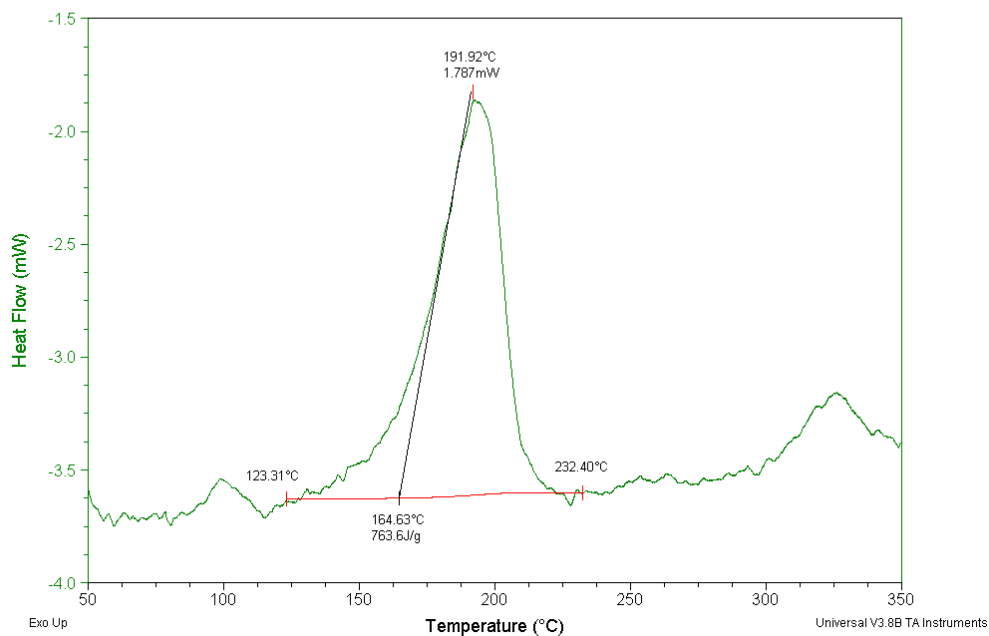
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Operator: DNS/DLK 57.28/57.02
Run Date: 3-Nov-03 12:01



Sample: BTTN 1%2NDPA DOPED ACTIVE CARBON
Size: 0.8500 mg
Method: 5°C/MIN FROM 50 TO 350°
Comment: N2,SEALED AL PANS,102903/418.49/157.75/0.8285/-16.69/0.4

DSC

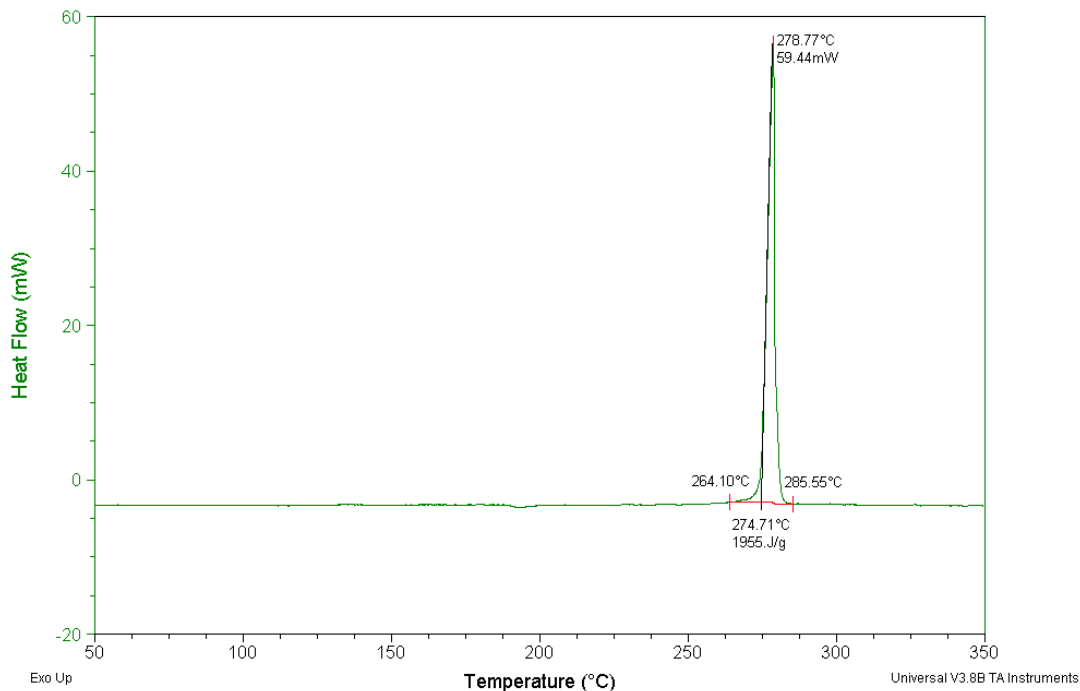
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Run Date: 4-Nov-03 09:23



Sample: HMX HOLSTON #87B240-021 @5°C/MIN
Size: 1.0400 mg
Method: 5°C/MIN FROM 35 TO 350°
Comment: N2,SEALED AL PANS,102903/418.49/157.75/0.8285/-16.69/0.4

DSC

File: D:\TA\Data\910-950\D1hmx.618
Operator: DNS/DLK 56.48/56.10
Run Date: 30-Oct-03 11:34



Sample: HMX IN ACTIVE C 3.62:3.52 @5°C/M
Size: 1.2700 mg
Method: 5°C/MIN 40-400°
Comment: IN N2,SEALED AL PAN,111803/418.31/157.81/0.8627/-13.93/0.4

DSC

File: D:\TA\Data\910-950\D1hmc-c.644
Operator: DNS/DLK 57.04/57.09
Run Date: 20-Nov-03 16:17

