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Construction Engineering Research Laboratory

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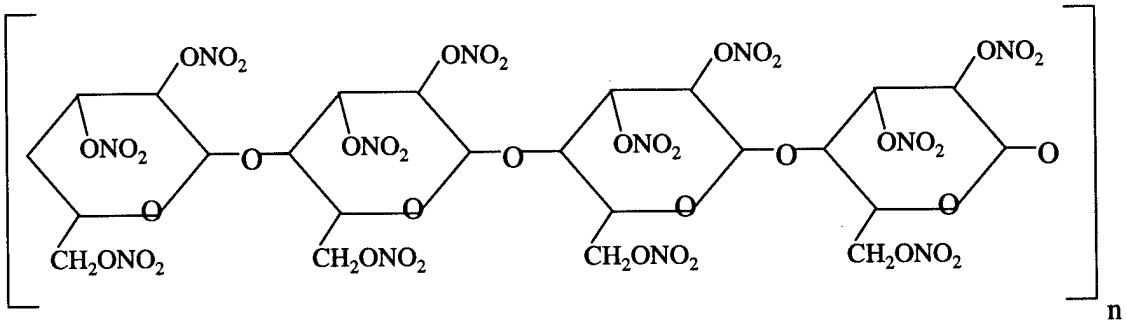
Sonolysis of Nitrocellulose Fines

by Donald Cropek and Brian Dankowski

May 2000



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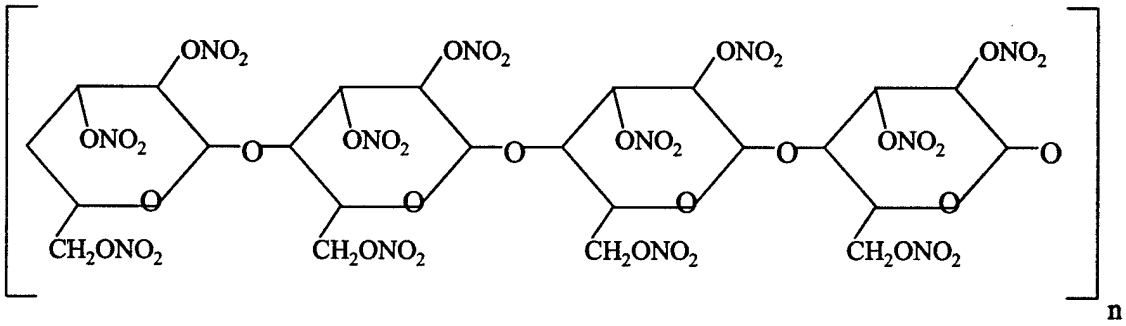

Foreword

This study was conducted by the Environmental Process Branch (CN-E) of the Installations Division (CN), Construction Engineering Research Laboratory (CERL). The work was performed under 611102BT25 "Environmental Research COE (6.1 Basic Research)," work unit J79, "Sonochemical Treatment of Nitrocellulose Fines."

The technical reviewer was Dr. Stephen W. Maloney (CN-E). The CERL Principal Investigator was Dr. Don Cropek, CN-E. Dr. Ilker Adiguzel is Chief, CN-E, and Dr. John T. Bandy is Chief, CN. The technical editor was Linda Wheatley, Information Technology Laboratory. The Acting Director of CERL is Dr. Alan W. Moore.

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1 Introduction

Background

The Army generates many types of unique wastes, primarily due to the manufacture of products with explosive or toxic characteristics. One of these products is nitrocellulose (NC), a macromolecule used in lacquers, inks, films, and membranes at low nitration levels and used in propellant formulations at high nitration levels (>12%). During the washing of NC fibers, fine particles of NC that do not settle can enter the wastewater. This wastewater becomes milky white due to the colloidal suspension of NC. Anywhere from 500 to 2000 pounds of the fine NC particles, known as NC fines, are released daily into the wastewater from NC production facilities (Kim and Park 1993). Currently, these facilities store the NC fines in holding tanks. The settlable solids are reused in secondary quality munitions. The remaining colloidal suspension is neutralized and discharged to a local waterway. If state regulations were interpreted differently, this discharge could be disallowed and the Army would require a new technique to treat the suspended fraction of NC fines. Research is underway to determine methods to treat or reuse the NC fines from this wastewater.

Objective

The objective of this study was to determine the effects of high intensity ultrasound on the NC macromolecule. This included development of methods to determine the degradation by-products, denitration studies, and molecular weight effects.

Approach

Two different types of NC were used in these experiments: an NC fines wastewater sample from an NC production facility and a sample of commercial NC nitrated below energetic levels. These solutions were sonolytically treated under different frequency conditions, insonation (sonication) times, sparge gases, solvents, and solution temperatures. Analyses for monitoring the progress of degradation included one or more of the following: liquid chromatography with

ultraviolet (UV)/visible absorbance detection, gas chromatography/mass spectrometry (GC/MS), gel permeation chromatography (GPC), capillary electrophoresis (CE), and pyrolysis/GC/MS (PY/GC/MS).

Scope

This work focused on understanding the effects that different experimental parameters had on the sonolysis of NC. Optimization of rates, development of reaction vessels, and cost analyses were not addressed.

Mode of Technology Transfer

It is anticipated that the results of this study will provide information and direction for applied research on the use of sonolysis to treat NC. Specifically, the results of this work will apply to compliance, pollution prevention, remediation, and demilitarization of aqueous waste streams containing NC. Because of its nonspecificity, sonolysis may also provide an additional method to treat other recalcitrant waste streams.

2 Nitrocellulose Treatment Technologies

Nitrocellulose

NC, the nitrated ester of cellulose, is a common energetic material used in smokeless powders and dynamites. The cellulose structure has three free hydroxyl groups (-OH) per six-membered glucose ring and each of these can be nitrated to $-O-NO_2$. For military applications, the cellulose is fully nitrated and is sometimes referred to as cellulose trinitrate containing over 13% nitrogen (N). For commercial applications, lesser degrees of nitration are required, typically below 12% N. The structure of NC is shown in Figure 1 (Yinon and Zitrin 1993; Urbanski 1964).

Because they bypass the collection systems, it is not surprising that NC fines are characterized by their small size. Workers have shown that these fines are polydisperse with most of the particles having a size of 40 microns or less (Kim and Park 1993).

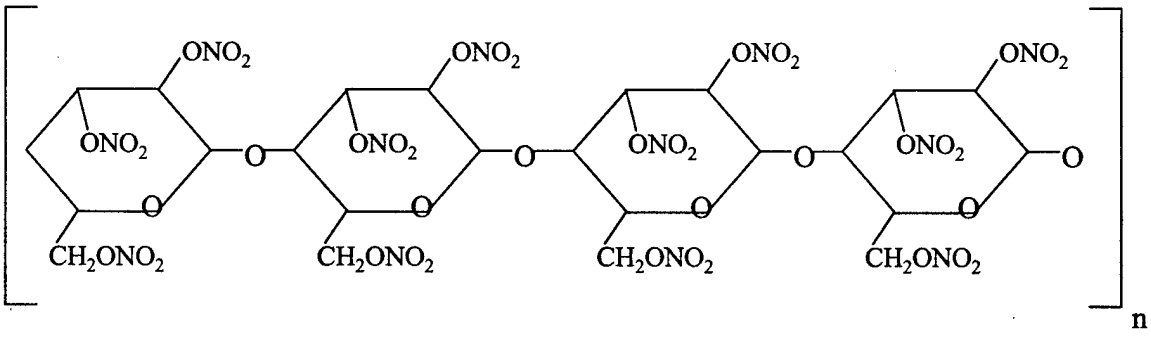

Figure 1. Structure of nitrocellulose (NC).

Current Treatment Methods

Methods to treat NC fines have been an active CERL research area for several years. A CERL-sponsored workshop at Purdue University reviewed several processes under investigation. These processes fall into two areas: physical/chemical treatment and biological treatment. Research results were presented in areas such as coagulation with cationic polymers (Peng, Park, and Kim 1993),

microfiltration (Shen, Park, and Kim 1993), selective denitration via pulsed laser (Yang and Ramsey 1993), alkaline hydrolysis (Alleman et al. 1993), and microbial and enzymatic degradation (Gallo et al. 1993; Duran, Kim, and Speece 1993). Composting studies, which are also biological in nature, have been studied on the filtered solids (Lowe 1993). Central to the study of each treatment is assessing its potential to replace open field incineration, the standard method of treating NC waste solids. This method is neither safe nor environmentally acceptable (Alleman et al. 1993).

The work reported here examines a degradation technique based on the application of high intensity sound waves to the aqueous NC system. The effect of ultrasound on the NC structure was examined.

Sonochemistry

Sonochemistry is defined as the chemical effects produced by subjecting a chemical reaction to sound waves (Bremner 1990). Ultrasound, with frequencies roughly between 15 kHz and 10 MHz, can have a drastic effect on chemical reactions. The mechanism that causes this effect is known as "acoustic cavitation."

This phenomenon begins with a sound wave impinging on a solution, which is merely a cyclic succession of compression and expansion phases imparted by mechanical vibration. During the solution expansion phase, small vapor-filled bubbles are formed at weak points in the solution, primarily at trapped gas pockets on particulate surfaces. These bubbles grow and contract in response to the expansion and compression phases of the cycle, respectively. Because the surface area of the bubble is greater during the expansion phase than during the compression phase, the bubble grows more than it contracts, resulting in an increase in the average bubble size over many cycles. Over time, the bubble reaches a critical size, depending on the ultrasonic frequency, when the pressure of the vapor within the bubble cannot withstand the external pressure of the surrounding solution. The result is a catastrophic collapse of the bubble with high velocity jets of solution shooting into the interior. This implosion process is known as acoustic cavitation. Extreme environments are produced in and near the bubble as a result. Suslick 1990 and 1989 give a more detailed explanation of acoustic cavitation.

Although many bubbles are produced, these bubbles are quite small. It is estimated that 4×10^6 bubbles/second/m^3 are produced (Suslick and Hammerton 1986). The bubbles are on the order of 10 to 200 microns in diameter, and they are short lived, with a lifetime near 10 microseconds. The bulk solution

conditions, therefore, remain relatively unaffected. The implosion of the bubble, however, causes enormous local effects. The temperature of the vapor within the bubble has been estimated to reach as high as 5000 °K (Suslick, Cline, and Hammerton 1986) with a concomitant pressure near 1000 atmospheres (Mason and Lorimer 1988). The principal result of these conditions in an aqueous solution is the breakdown of water vapor in the bubble into hydrogen and hydroxyl radicals. These radical species are usually the impetus for interesting chemical effects. Therefore, the three principle sonochemical conditions that induce chemical effects are radical attack, high temperature pyrolysis inside the bubbles, and supercritical water oxidation in a small shell around the bubble.

Uses of Sonochemistry

The unusual microenvironments created during acoustic cavitation permit a variety of uses for ultrasound. These uses include homogenization and cell disruption in the biological field; dissolution and mixing in chemistry; soldering and welding in metal working; degreasing and emulsification in industry, as well as uses in geology and medicine (Bremner 1990). Novel chemical applications result from the catalytic effects of sonochemistry. These applications include the creation of new compounds such as iron carbonyl compounds (Suslick et al. 1991), new and more effective catalysts (Suslick and Casadonte 1987), and greater rates and yields on chemical reactions (Luche 1990). Research areas such as these provide the majority of sonolytic applications. In the past several years, the use of sonochemistry as a destruction technique has blossomed.

Several researchers have experimented with using ultrasound expressly for the degradation of organic contaminants. Nearly all such research is performed in aqueous media for relevance to treating contaminated ecosystems. Examples include destruction of chlorinated compounds (Francony and Petrier 1996; Drijvers et al. 1996), phenolic compounds (Petrier et al. 1994; Serpone et al. 1982), hydroxyanisoles and resorcinol (Takizawa et al. 1996), sodium hypochlorite (Mason et al. 1996), iodide and bromide (Gutierrez, Henglein, and Ibanez 1991), arylalkanes (Soudagar and Samant 1995), and glyceraldehyde (Fuchs and Heusinger 1995). These species are affected by either the sonolytically produced radical species or high temperatures. Nitro compounds are of special interest. Studied systems include nitrotoluenes in the presence of potassium permanganate (Soudagar and Samant 1995), p-nitrophenol (Kotronarou, Mills, and Hoffmann 1991), 2,4,6-trinitrotoluene (TNT) (Hoffmann, Hua, and Hochemer 1996), and nitrobenzene (Cropek and Kemme 1998). All studies observed denitration of the molecule with concomitant production of NO^{2-} and NO^{3-}.

The ultrasonic applications pertinent to this work are polymerization and depolymerization. Polymerization by ultrasonic irradiation is primarily due to the production of radical species of either the solvent or the monomeric precursors. The radical species have facile recombination kinetics to create longer chain macromolecules (Bremner 1990).

Depolymerization involves the breakdown of macromolecules. Depolymerization occurs, not by chemical effects, but by the mechanical forces that arise during cavitation. It is believed that two primary mechanical forces contribute to the depolymerization action. The bubbles formed during irradiation grow and shrink in size in response to the rarefaction and compression cycles of the incident acoustic wave. This process creates the first type of force, shear stress, which arises from the movement of solvent molecules around the pulsating bubbles. When the bubble undergoes collapse, intense flows of solvent move toward the bubble center followed by a reactive wave of solvent away from the implosion. This shock wave provides the second type of force. A macromolecule present in the solution will experience the extreme turbulence generated by cavitation. The solvent velocity gradients are strong enough to cleave chemical bonds. The entire macromolecule has sufficient inertia to prevent it from moving in its entirety in response to the solvent flows and only local interior sections move in rapid response. The usual model has the polymeric species anchored at one or both ends with the mechanical forces acting on the interior backbone chain, thus stretching and breaking the molecular chain (Price 1990).

Examples of sonolytic degradation of polymers include dextran (Lorimer et al. 1995); starch, gelatin, and gum arabic (Szalay 1933); polystyrene, poly (methylmethacrylate), and polypropylene (Tabata et al. 1980); and poly (dimethyl siloxane) (Shaw and Rodriquez 1967). Other research is noted in Price (1990). In all cases, the general behavior is a decrease in viscosity related to a reduction in the molecular weight of the initial polymer.

3 Experimental Parameters

Chemicals

All water used for either the liquid chromatographic (LC) mobile phase or as a solvent was distilled and deionized with a Milli-Q Plus system (Millipore Systems, Bedford, MA). The acetonitrile used as a component of the LC mobile phase was high performance liquid chromatography (HPLC) grade (Sigma Chemicals, St. Louis, MO, 99.93+% HPLC grade). The tetrahydrofuran (THF) used as a solvent for the gel permeation chromatography system was HPLC grade (Sigma, 99.9+%). THF, acetonitrile, and water were all filtered before use with a 0.45-μm pore size nylon filter (Micron Separation, Inc., Westboro, MA). Mobile phase solvents passed through a four channel solvent degasser (Degassit, MetaChem Technologies Inc., Torrance, CA) before reaching the inlet pumps. Liquid/liquid extractions were performed with methylene chloride (Aldrich Chemicals, Milwaukee, WI, 99.9+% capillary GC grade). The acetone used as a solvent was pesticide grade (Fisher Scientific, Pittsburgh, PA). The nitrocellulose sample was either actual NC fines wastewater or 11.5% N nitrocellulose (Hercules, Inc., Wilmington, DE). Argon, helium, and nitrogen gases were all ultra-high purity (AGA Specialty Gas, Danville, IL, 99.999%).

Analytical Equipment

After sonication, the resultant NC samples were analyzed first by HPLC using an LC Module Plus 1 (Waters Corporation, Milford, MA) consisting of a Model 600 HPLC pump and a Model 486 UV/visible absorbance detector. The detection wavelength was 254 nm and the LC column was an ABZ+ column, 25 cm by 4.6 mm, with a 5-μm diameter particle size (Supelco, Bellefonte, PA). In all cases, the mobile phase was a water/acetonitrile mixture (70:30) with a flow rate of 1 mL/minute and an injection volume of 10 μL.

The Capillary Ion Analyzer (CIA), manufactured by Waters, was used to identify any ions that may have been produced by sonolysis. Ionic compounds are separated by capillary electrophoresis (CE) and identified by comparison with standards. The electrolyte used was 25 mM sodium phosphate/1 mM OFM hydroxide concentrate (Waters), pH = 8. The system used a Waters capillary column, 75

μm (i.d.) by 375 μm (o.d.) x 60 cm. Samples were run under ambient temperature (25 °C) with negative polarity and a 15 kV potential. Sampling was hydrostatic for 30 seconds and detection was by direct UV at 185 nm.

Further identification of sonolytic by-products was done using a GC/MS system consisting of an HP 6890 Series Plus GC, a 5973 Mass Sensitive Detector, and the G170113A Enhanced ChemStation software (Hewlett Packard, Palo Alto, CA). The column was an HP-5MS (Hewlett Packard), 30 m in length by 0.25 mm (i.d.) by 0.25 μm film thickness, with a coating of cross-linked 5% phenyl/95% methyl silicone. The injector was operated in splitless mode and set at 200 °C. The MS source was set at 230 °C and scanned from 30 to 250 amu. The method used an initial oven temperature of 40 °C for 3 minutes, ramped at 10 °C/minute to 250 °C, and held for 6 minutes. Samples injected were between 1 and 5 μL and the total analysis time was 30 minutes.

A GPC system was used to observe the effect sonolysis had on the molecular weight of NC. The system comprised a Model 510 HPLC pump (Waters), a Millipore filter housing unit with Whatman Anodisc 0.2-μm membrane filters (Whatman, Inc., Clifton, NJ), two Shodex 6PC KF-806M columns connected in series (Showa Denko, Tokyo, Japan), a miniDawn light scattering detector (Wyatt Technology, Santa Barbara, CA) using 690 nm wavelength detection, and an Optilab refractometer (Wyatt Technology). The solvent used for the system was always THF, and samples analyzed on the GPC were diluted to a concentration of approximately 5 mg/mL with THF. The NC dn/dc* value used for the calculations was 0.079, and instrument calibration was done using a 65,000 molecular weight (Mw) polystyrene standard (Pressure Chemical, Pittsburgh, PA). Astra for Windows (Version 4.5) served as the operating software program.

The PY/GC/MS analytical technique is used to study materials that are not amenable to direct injection into the GC/MS, such as polymers, paints, oils, microorganisms, and soil (Wampler 1995). The GC/MS serves as a monitoring instrument to collect and characterize the thermal degradation products from pyrolysis. The instrumentation for laboratory pyrolysis consisted of a CDS Pyroprobe 2000 (CDS Analytical, Inc., Oxford, PA) interfaced onto an HP 5890 GC/5970 MS (Hewlett Packard). The helium carrier gas flowed through the pyrolysis chamber and directly into the injection port of the GC. This arrangement

* dn/dc = change in refractive index over change in concentration.

had the advantage of sweeping all gaseous pyrolysis by-products into the GC/MS for analysis. The by-products are separated by a two-column system. A Pora-PLOT Q column (Chrompack, Raritan, NJ), 50 m by 0.32 mm (i.d.) by 10 μm film thickness, was used for separation of the low molecular weight species and a Molsieve 5A column (Chrompack), 25 m by 0.32 mm (i.d.), was used for separation of light permanent gases. Approximately 2 mg of a solid sample was loaded into a quartz tube plugged with quartz wool to keep the sample positioned in the pyrolytic hot zone. This prepared tube was then placed inside a platinum wire coil on the CDS Pyroprobe 2000. The probe was inserted into the pyrolysis chamber. A 20-minute waiting period was required after inserting the probe to allow the entrant air to pass through the GC/MS. Heat was applied to the platinum coil through electric resistance, which pyrolyzes the sample. The by-products are swept from the chamber into the GC/MS. The pyrolysis temperature program consisted of heating the sample from 100 °C to 1200 °C at a rate of 20 °C per millisecond and holding this final temperature for 100 seconds. The pyrolysis chamber was maintained at 120 °C, which was hot enough to ensure that volatile by-products did not accumulate within the chamber, but not hot enough to thermally degrade the sample before the probe was fired. After pyrolysis, the GC oven program began at 40 °C for 2 minutes followed by heating to 200 °C at a moderate 10 °C/min. The oven was held at 200 °C for 2 minutes to ensure complete elution of analytes from the column. Blank pyrolytic experiments were run between each sample to ensure no carryover of by-products between runs.

Ultrasonic Equipment

The ultrasonic irradiation of aqueous solutions was performed using three different systems. The first was a VibraCell Model 600 direct immersion ultrasonic horn (Sonics and Materials, Danbury, CT) that was operated at 20 kHz with a maximum power output of 600 W/cm^2. The setup used a Suslick vessel, a glass test tube with three arms spaced 60 degrees apart located below the mouth of the test tube. The ultrasonic horn was immersed directly into the solution through the top of the test tube to form a tight seal. The vessel was placed into a coolant bath (Grant Instruments, Science/Electronics, Dayton, OH) held at 5 °C. Two of the arms were used for the introduction and exit of purge gas when desired. The third arm was sealed and served no purpose in these experiments. When air was the purge gas, the arms were left uncapped for free passage of air into the system. Samples were irradiated in a pulsed manner, 1 second on and 1 second off, for a set amount of time at an amplitude setting of 50%. Approximately 15 mL of solution was irradiated per experiment.

The second system used a transducer system operating at 660 kHz with a power output between 240 and 960 W (Ultrasonic Energy Systems, Panama City, FL). A specially designed jacketed vessel made by Ace Glass (Vineland, NJ) was affixed to the transducer plate using Dow Corning silicone sealant (Cropek and Kemme 1998). The reaction vessel was filled with approximately 750 mL of solution, and cooled to 5 °C using coolant water pumped through the jacket of the vessel. The sound waves traversed the length of the vessel in a plane wave, hit the concave end of the vessel, and reflected back to a focal point down about two-thirds the length of the reaction vessel. The vessel was equipped with three quartz windows for optical interrogation and several different circular openings at the top of the vessel for various probes. The solution was irradiated using repetition rate and pulse width settings of 2.5 and an amplitude setting of 6. These settings corresponded to a pulsed irradiation of approximately 0.2 seconds on and 3.2 seconds off.

The third system consisted of an LVG 60 radio frequency generator with a USW 51 Ultrasonic Transducer (AlliedSignal ELAC Nautik, Kiel, Germany). This instrument operates at a frequency of 360 kHz or 1.07 MHz, with a maximum power output of 200 W, and an intensity range of 0-8 W/cm^2. The system included a cylindrical reaction chamber (approximately 600 mL) with a cooling jacket. The reaction chamber was mounted directly to the transducer in the vertical position using a large o-ring and clamp.

Analytical Sample Preparation and Methodology

Two types of NC samples were used in these experiments. An actual NC fines wastewater was available and aliquots of this colloidal solution were sonicated after thorough mixing. This milky solution was approximately 200 ppm NC. A simulated version of NC fines wastewater was made by adding 11.5% N NC to water, resulting in a final concentration between 500 and 1000 ppm NC. For the 20 kHz horn experiments, 15 mL of solution was used, and approximately 600 mL of solution was required for the AlliedSignal and the Ultrasonic Energy Systems set-ups.

After sonolysis of a sample, a choice of analytical techniques was used to study the results. LC is used to determine if any small products, organic or inorganic, are cleaved from the NC molecule. Some products, however, may have little absorption at 254 nm (e.g., those without conjugation or aromaticity). GC/MS is used for identification of organic fragments extractable by methylene chloride. CE is used for analysis of inorganic ions in the aqueous phase. Any denitration of NC will be noted by an increase in the nitrate/nitrite peaks in CE. While

these three techniques will not analyze NC, the two remaining methods can directly probe the NC macromolecule. GPC is capable of noting the molecular weight changes of NC due to sonolysis. Pyrolysis provides a fingerprint of the molecular composition of NC to provide information on changes in bond configuration and constituents.

Although not all techniques were generally utilized for each sample, the following description is a brief procedure for each method. After sonication, a 1 mL portion of the sample was filtered with a 0.2 μm filter to remove NC and a 10 μL injection was analyzed by LC. For CE, another 1 mL portion of the sample was filtered and analyzed. The remaining aqueous sample was extracted three times with methylene chloride. NC is not soluble in methylene chloride. These extractions were combined, filtered if necessary, concentrated, and a 1 μL injection was analyzed by GC/MS. The aqueous fraction was vacuum filtered to collect the polymer. This solid portion was washed with water several times and dried overnight in an oven at 105 °C. After cooling, a portion of the solid was studied by pyrolysis. Another portion of the solid was dissolved in THF for a solution concentration of 5 mg/mL, filtered, and analyzed by GPC.

4 Results and Discussion

A colloidal suspension of the NC macromolecule is expected to provide an interesting system to investigate sonochemical effects. Nucleation sites for cavitation are provided by gas pockets trapped on solid surfaces (Atchley and Crum 1988). The NC molecule may therefore localize the cavitation events in proximity to itself. Expected and desired sonochemical effects include denitration of the NC and breakdown of the polymeric chain. Studies on macromolecular degradation by ultrasound show that the molecular weight decreases asymptotically to a lower bound, after which continued polymer chain ruption does not occur (Price 1990). The data provided below test for denitration and depolymerization of NC.

Several different experimental parameters were investigated based on known sonolytic effects from the literature. These included insonation time (sonication time), frequency effects, sparge gas, solvent effects, and solution temperature. The results are presented below with accompanying data.

Initial Analysis of Nitrocellulose

Both the actual NC fines sample and the simulated NC fines sample were analyzed by all the analytical methods to provide baseline data. Figures 2a and 2b show the LC data from the samples. The chromatogram for the simulated NC fines water shows only the injection peak, which is not surprising considering that NC is water insoluble and this solid has been washed with water numerous times during production. The actual NC fines sample was already in a portion of wastewater from NC production. The aqueous portion has only one large initial peak in the chromatogram. Since this peak elutes just before the injection peak, it has no retention in this LC system and is likely ionic in nature. It is also a good absorber of 254 nm light, and is likely either nitrate or nitrite ions from the production or progressive aging of NC. Figures 3a and 3b show the retention behavior of the nitrate ion at 2.0 minutes and the nitrite ion at 2.0 minutes, respectively. These ionic species co-elute just before the injection volume at 2.2 minutes and have appreciable absorbance at 254 nm.

CE data for the initial NC samples are shown in Figures 4a and 4b. As expected from the LC data, the simulated NC fines sample has no ionic peaks while the

actual NC fines sample has two distinct peaks. Using standards, it is known that peak 1 is the nitrite ion and peak 2 is the nitrate ion. Therefore, the large peak observed in Figure 2b is likely a combination of nitrate and nitrite ions. CE analysis of the aqueous portions of the NC samples after sonolysis will allow monitoring of the denitration process.

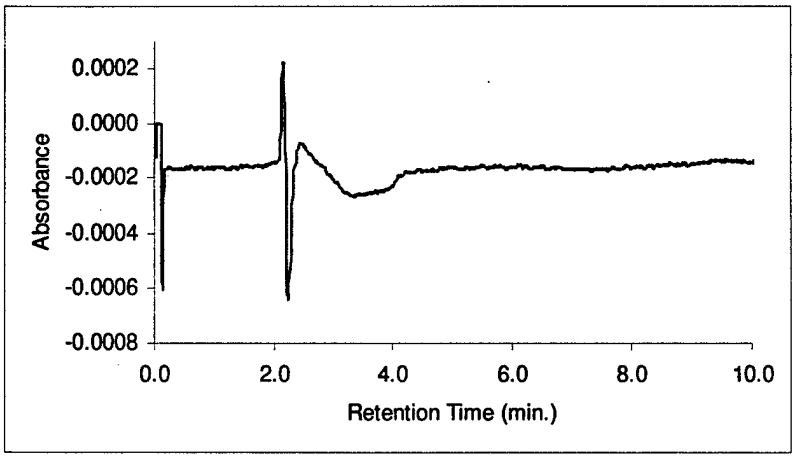

Figure 2a. LC of simulated NC fines water after filtration.

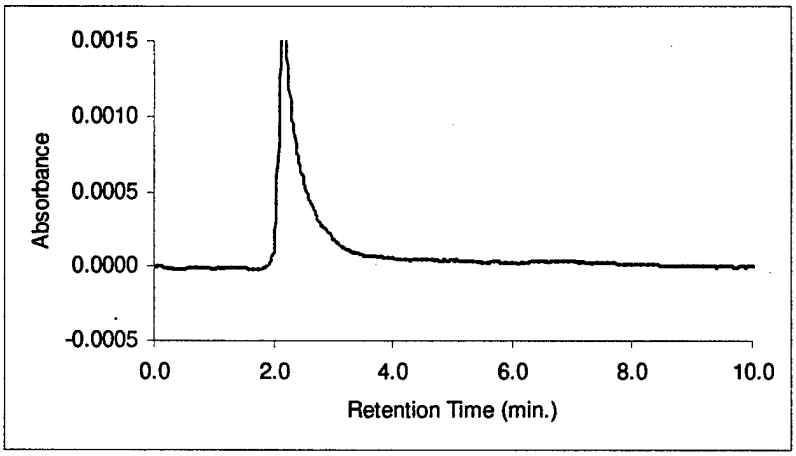

Figure 2b. LC of actual NC fines water after filtration.

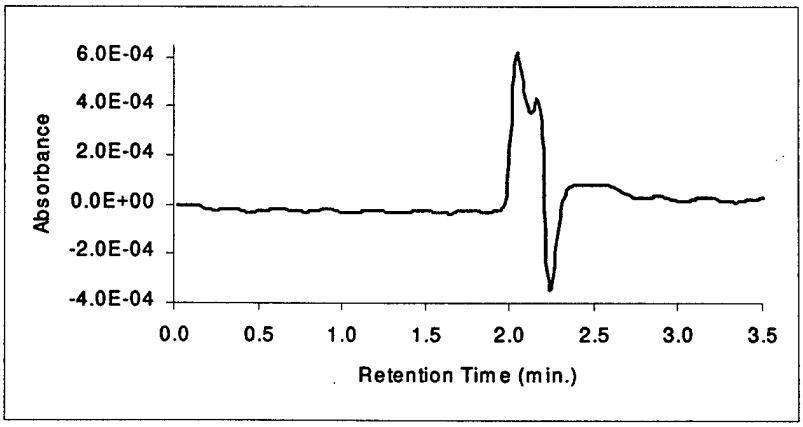

Figure 3a. LC of nitrate standard.

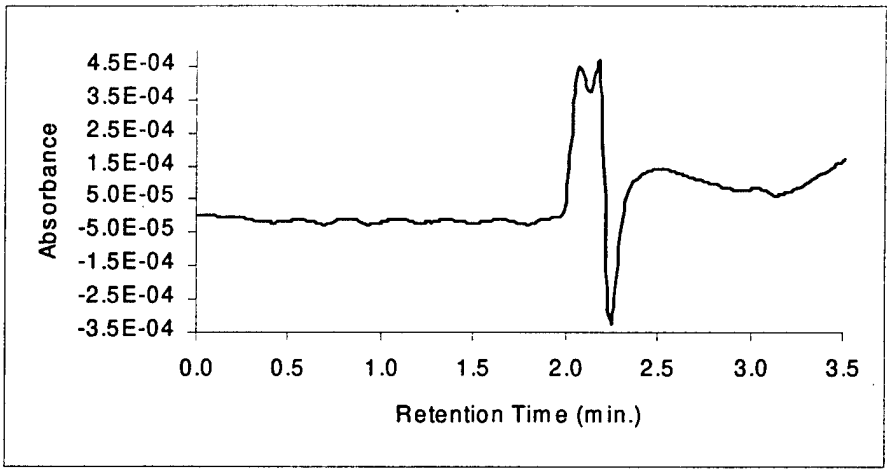

Figure 3b. LC of nitrite standard.

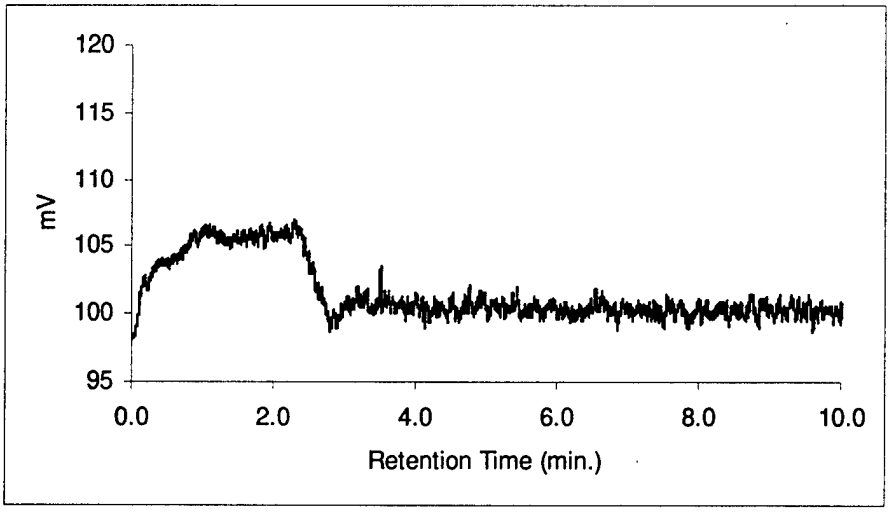

Figure 4a. CE of simulated NC fines water after filtration.

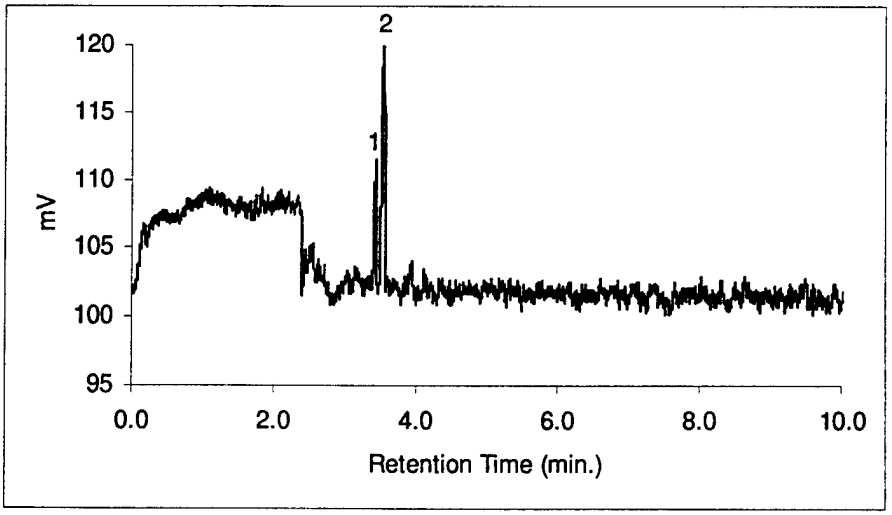

Figure 4b. CE of actual NC fines water after filtration.

Samples of the simulated NC fines and the actual NC fines were extracted with methylene chloride, concentrated, and 1 μL was injected onto the GC/MS. Figures 5a and 5b are the chromatograms of the organic constituents extractable from the simulated NC waste and the actual NC fines, respectively. Since NC is not soluble in methylene chloride and its mass is so large, it could not be extracted or analyzed by GC/MS. The peaks present in 5a are unfortunately due to a dirty system and all are background siloxane peaks. These figures show that no extractable fragments were in the original NC samples.

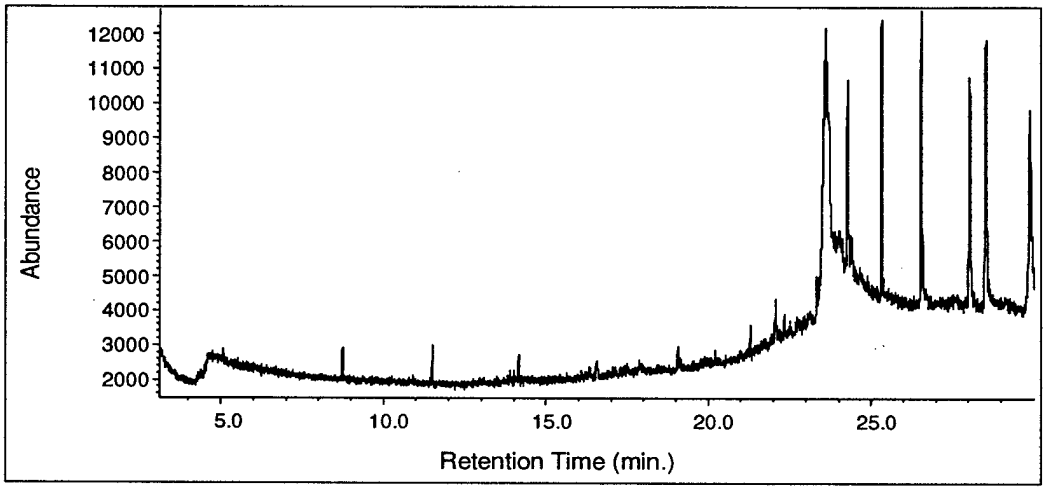

Figure 5a. GC/MS of methylene chloride extraction of simulated NC fines water.

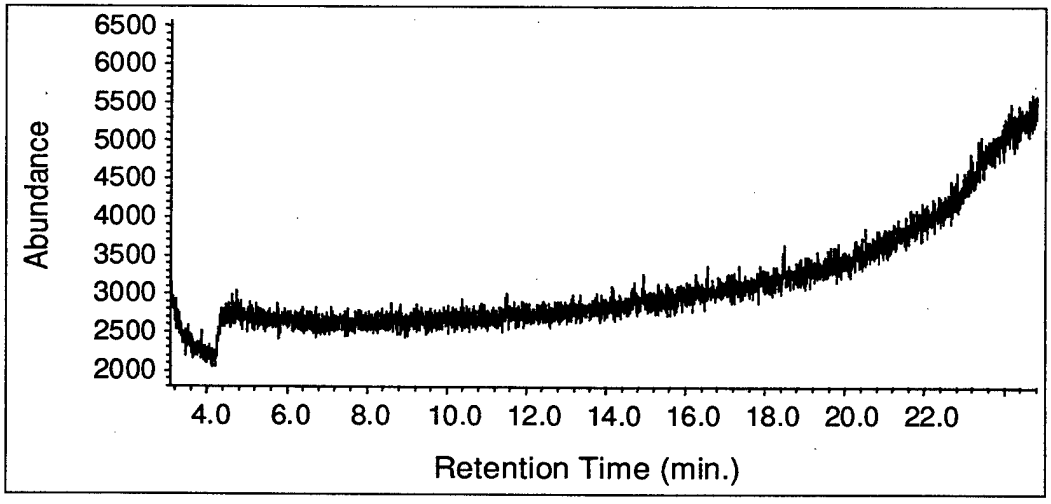

Figure 5b. GC/MS of methylene chloride extraction of actual NC fines water.

Figures 6 through 8 present pyrolysis data from the thermal decomposition of unnitrated cellulose, actual NC fines, and 11.5% nitrated NC. All are washed and dried before analysis. The cellulose, Figure 6, has the most complex pyrogram. The numbered peaks are identified in Table 1. The key feature to note in the pyrolysis of cellulose is the lack of nitrogen-containing by-products as expected. In contrast, actual NC fines (Figure 7) and 11.5% nitrated NC (Figure 8)

have substantial contributions from nitrogenous by-products. The numbered peaks in Figures 7 and 8 are also identified in Table 1; however, the nitrogen-containing by-products are denoted by letters for emphasis. The primary pyrolytic species for evidence of nitration are HCN (peak B) and NO (peak F), clearly visible in both pyrograms. The two NC samples produce similar pyrograms, but the commercial 11.5% nitrated NC has more peaks than the NC fines. Formic acid is the dominant peak in the 11.5% nitrated NC pyrogram and is not produced by the actual NC fines. Pyrolytic analysis of NC that has been sonolyzed will allow determination of denitration by the observation of loss of the nitrogen-containing by-products.

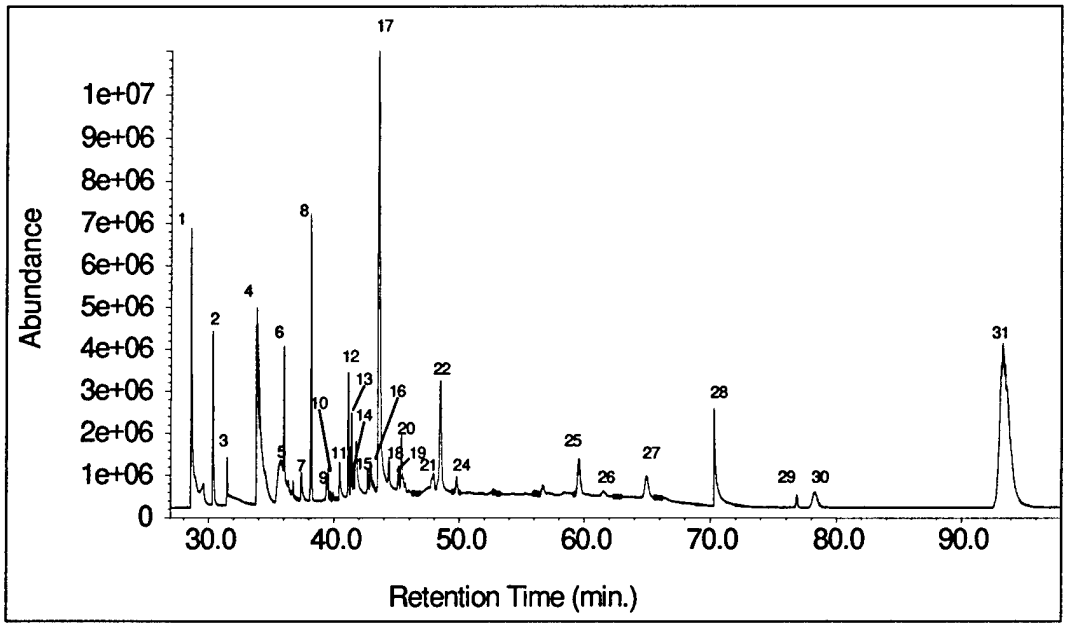

Figure 6. Pyrogram of cellulose.

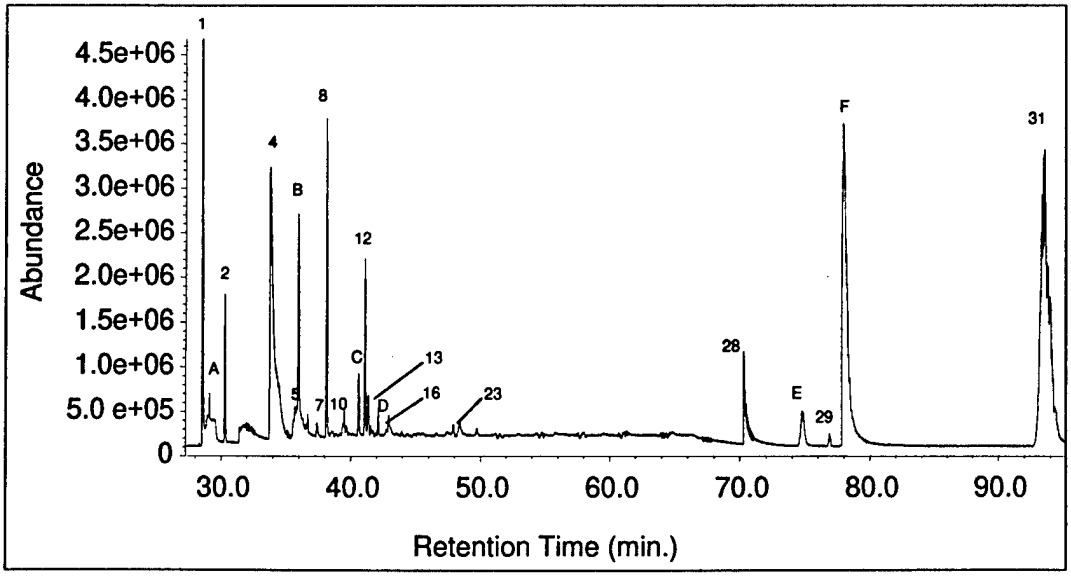

Figure 7. Pyrogram of actual NC fines.

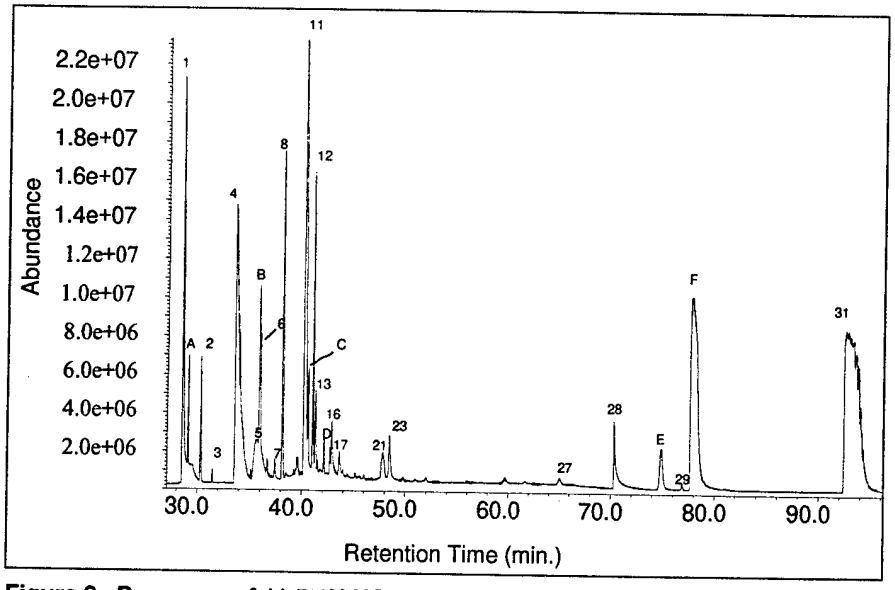

Figure 8. Pyrogram of 11.5%N NC.

Table 1. Peak identification of pyrolytic by-products of cellulose (Figure 6), actual NC fines (Figure 7), and 11.5%N NC (Figure 8).

Peak Label	Cellulose	Actual NC fines	11.5%N NC
1	CO_2	CO_2	CO_2
A		N_2O	N_2O
2	Ethene	Ethene	Ethene
3	Ethane		Ethane
4	H_2O	H_2O	H_2O
5	Formaldehyde	Formaldehyde	Formaldehyde
B		HCN	HCN
6	Propene		Propene
7	Methanol	Methanol	Methanol
8	Acetaldehyde	Acetaldehyde	Acetaldehyde
9	2-Methyl-1-propene		
10	1,3-Butadiene	1,3-Butadiene	
11	Formic acid		Formic acid
C		Acetonitrile	Acetonitrile
12	2-Propenal	2-Propenal	2-Propenal
13	Furan	Furan	Furan
14	Acetone		
D		2-Propenenitrile	2-Propenenitrile
15	2-Propen-1-ol		
16	Acetic acid	Acetic acid	Acetic acid
17	Hydroxyacetaldehyde		Hydroxyacetaldehyde
18	2-Methyl-2-propenal		
19	3-Buten-2-one		
20	2,3-Butanedione		
21	2-Butenal		2-Butenal
22	1-Hydroxy-2-propanone		
23		Methyl formate	Methyl formate
24	Benzene		
25	Propenal		
26	Toluene		
27	2-Furancarboxaldehyde		2-Furancarboxaldehyde
28	Background air	Background air	Background air
E		N_2	N_2
29	Background air	Background air	Background air
F		NO	NO
30	CH_4		
31	CO	CO	CO

Since the major effect of sonication on large macromolecules is depolymerization, GPC data are important to assess the reaction. Analysis of the polystyrene standard (Mw = 65000) on this system with a dn/dc value of 0.183 resulted in a molecular weight measurement of 64350 and a polydispersity value of 1.006. These results demonstrate an accuracy of the system for molecular weight analysis of about 1%. Some of the actual NC fines were filtered from the sample, dissolved in THF, re-filtered, and analyzed by GPC. The system calculated a molecular weight value of 89190 and a polydispersity of 1.751. The same filtration and dissolution procedure was used to obtain a sample of the 11.5% N NC suitable for GPC analysis. This commercial NC gave a molecular weight value of 73490 and a polydispersity of 1.273.

Insonation Time Dependence at 20 kHz

This section examines the sonolysis of NC at 20 kHz for different sonolysis times. Insonation times were 1 and 5 hours. Two samples of actual NC fines were sonicated for these times while being argon sparged and cooled to 5 °C. The aqueous solution was analyzed by LC. These data are shown in Figures 9a and 9b. In comparison to the LC before sonication (Figure 2b), it is noted that the 1-hour experiment in Figure 9a has a shoulder appearing at 2.4 minutes. In the 5-hour run in Figure 9b, this peak is now dominant. It has a different retention time than the original nitrate/nitrite peak. This new peak also prefers the aqueous phase and is likely small and ionic, with a substantial absorption at 254 nm. In an effort to identify this peak, the 5-hour sonicated solution was analyzed by CE. The results are shown in Figure 10. The familiar nitrite and nitrate peaks are present but no new peak has appeared, therefore, the new peak is not a simple anionic compound. Furthermore, since neither of the inorganic nitrogen anions grow with increasing sonication time, there is no evidence of denitration of the NC polymer. Sonolysis of water produces hydrogen peroxide by recombination of hydroxyl radicals (Bremner 1990). Analysis of H_2O_2 by LC produces a peak (not shown), which co-elutes with nitrate and nitrite, also eliminating this as the identification of the new peak.

A sample of the actual NC fines was filtered to remove all NC. This sample was analyzed by LC before and after sonolysis for 1 hour, identical to conditions described in the previous paragraph. Figures 11a and 11b show the chromatograms for this experiment. They are quite similar and no new peak is observed at 2.4 minutes after sonication. This result indicates that the new peak noted above is not derived from sonolysis of the free nitrates/nitrites or the water, but is derived from the NC molecule.

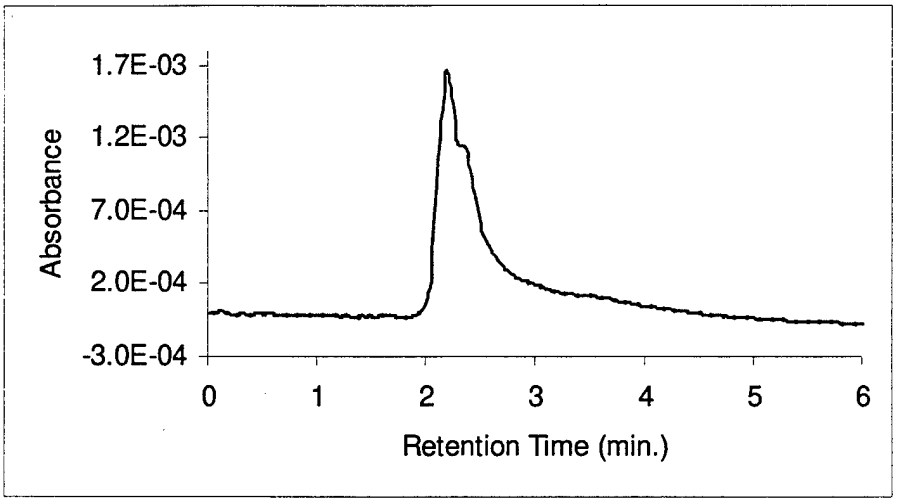

Figure 9a. LC of actual NC fines after sonication for 1 hour at 20 kHz.

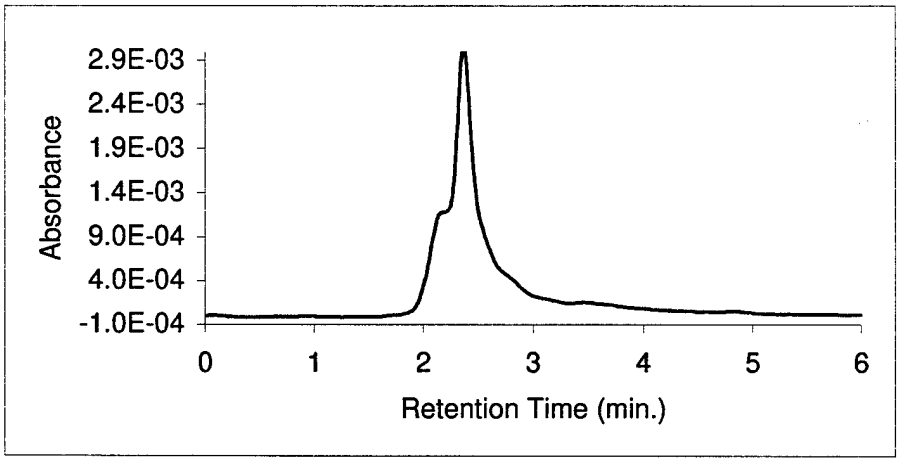

Figure 9b. LC of actual NC fines after sonication for 5 hours at 20 kHz.

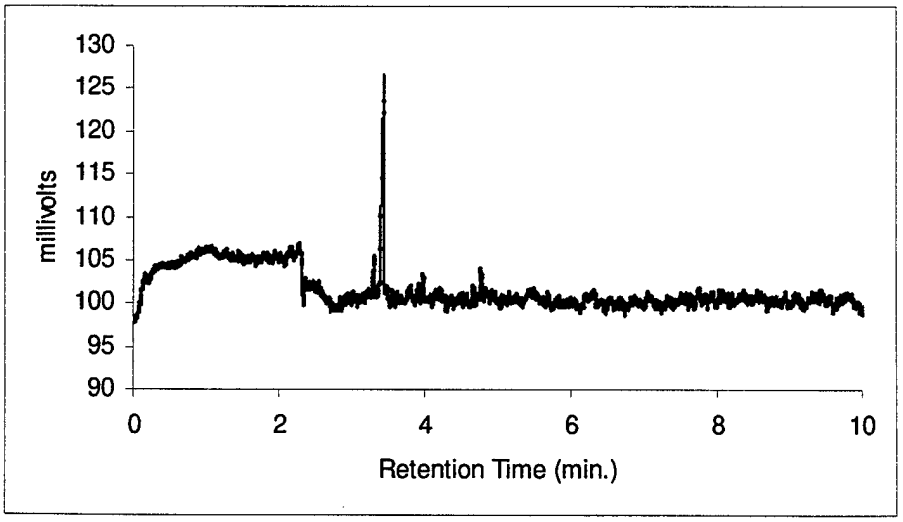

Figure 10. CE of filtered actual NC fines after sonication for 5 hours at 20 kHz.

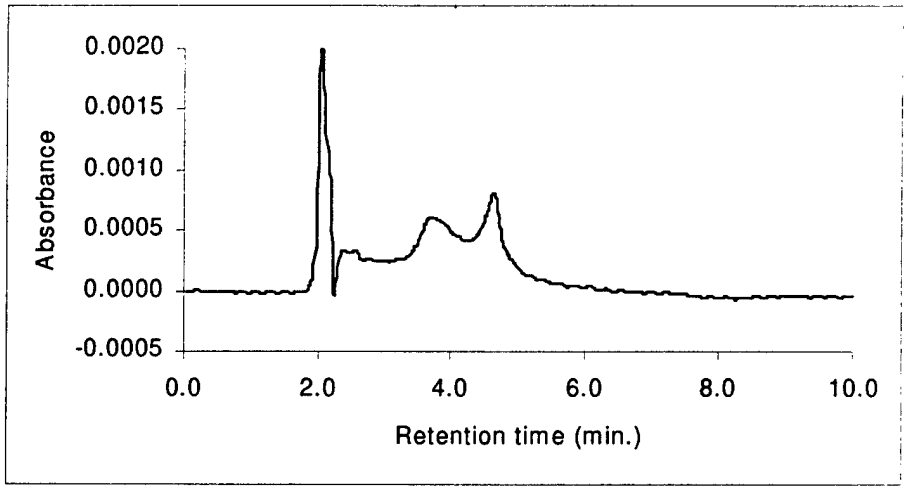

Figure 11a. LC of filtered water from actual NC fines before sonication.

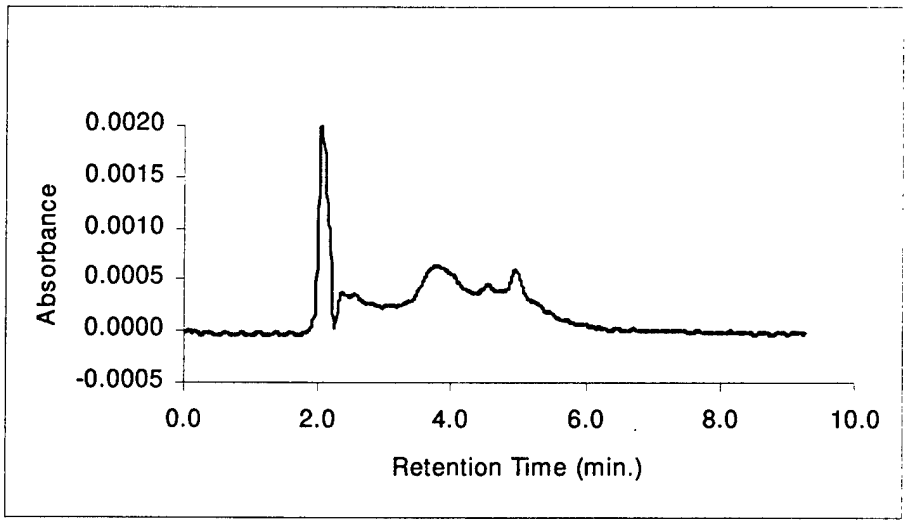

Figure 11b. LC of filtered water from actual NC fines after sonication.

The sonicated solutions from Figure 9 were extracted with methylene chloride, concentrated, and a sample of this organic portion was analyzed by GC/MS. Figures 12a and 12b are the chromatograms for the 1-hour and 5-hour experiments, respectively. All observed peaks are septum degradation and column siloxanes. The two chromatograms have no common peaks. Therefore, the sonolytic by-product observed in Figure 9 is neither extractable by methylene chloride nor analyzable by GC/MS. There is no evidence of any organic sonolytic by-products from the NC polymeric chain.

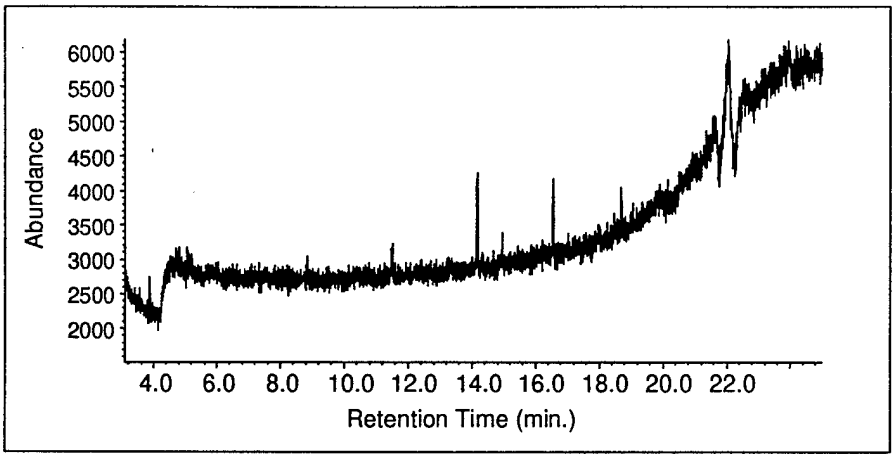

Figure 12a. GC/MS of methylene chloride extraction of actual NC fines sonicated for 1 hour.

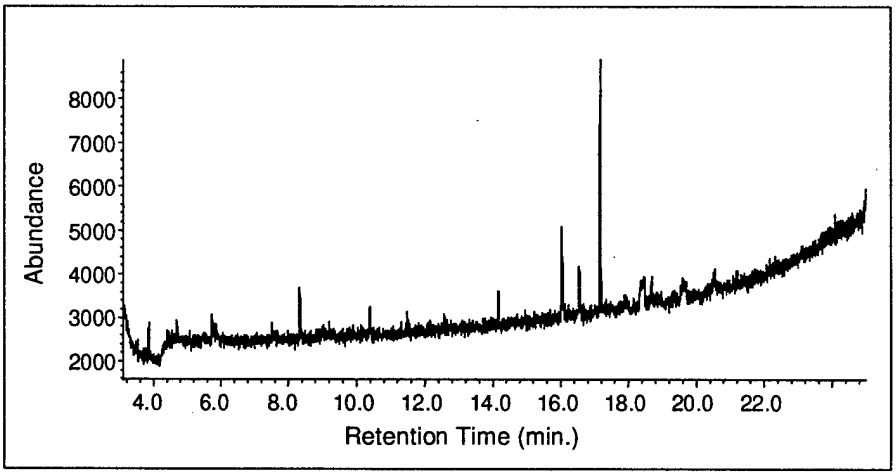

Figure 12b. GC/MS of methylene chloride extraction of actual NC fines sonicated for 5 hours.

Frequency Dependence

It has been shown that degradation rates increase at higher frequencies up to a certain limit, after which the rate actually decreases (Price 1990). This effect is a trade off between the number of cavitation events and the intensity of each cavitation event. Increasing the frequency increases the number of cavitation events. At higher frequencies, however, bubbles have less time to grow and collapse in response to the faster cycling of the pressure wave, which lessens the intensity of each cavitation event.

Figures 13a, 13b, and 13c show three LC chromatograms illustrating ultrasonic frequency effects on the NC solutions. Samples of the simulated NC solution were sonicated with 20 kHz (Figure 13a), 660 kHz (Figure 13b), and 1.07 MHz (Figure 13c). All samples were sonicated for 1 hour at 5 °C with an argon sparge.

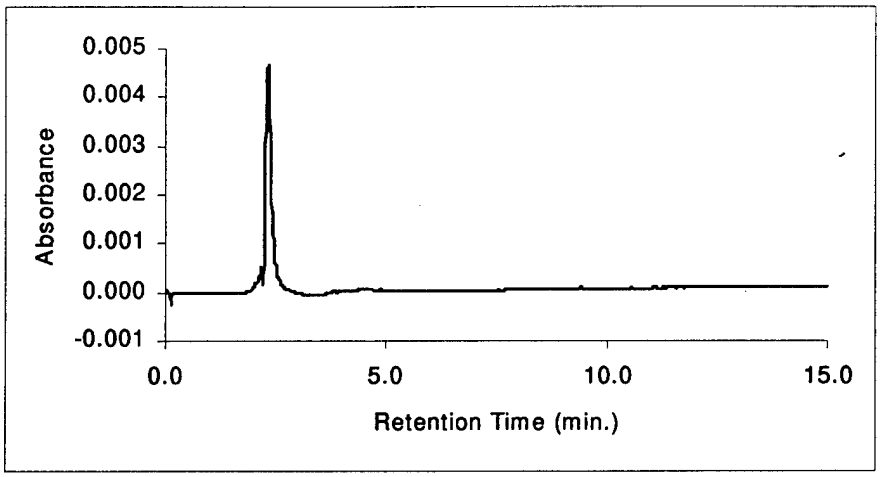

Figure 13a. LC of simulated NC fines wastewater after sonication for 1 hour at 20 kHz.

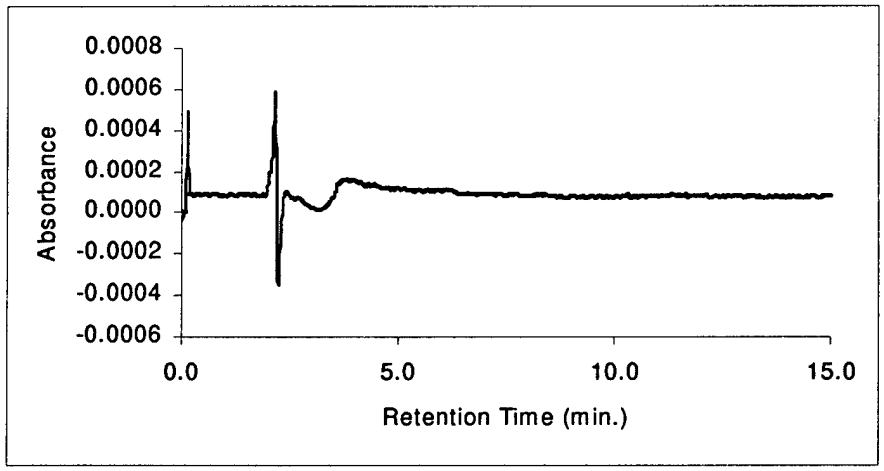

Figure 13b. LC of simulated NC fines wastewater after sonication for 1 hour at 660 kHz.

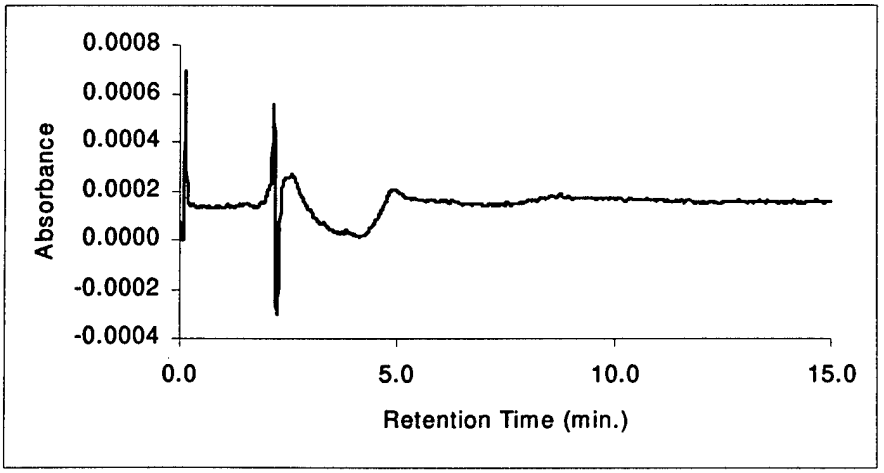

Figure 13c. LC of simulated NC fines wastewater after sonication for 1 hour at 1.07 MHz.

Only the 20 kHz frequency shows an effect. The large sonolytic by-product peak at 2.4 minutes has been noted above from the sonication of the actual NC fines (Figure 9). This by-product is not formed at higher frequencies. Therefore, production of this by-product from the NC requires cavitation for the mechanical forces to degrade polymers rather than merely the application of sound waves. Therefore, further work with higher frequencies was not performed.

A sample of the solid NC after sonolysis at 20 kHz for 1 hour (Figure 13a) was collected by filtration, washed several times with water, and dried at room temperature. This solid was analyzed by pyrolysis and GPC. The pyrogram (not shown) is nearly identical to the initial pyrogram for 11.5% nitrated NC in Figure 8. There is a slight decrease in the abundance of acetaldehyde, formic acid, and 2-propenal relative to the CO_2 abundance but nothing to assist in identification of the unknown sonolytic by-product or to indicate any breakdown of the NC. The molecular weight value of this NC was 84880, an increase in molecular weight from the initial value of 73490. Apparently, more polymerization than depolymerization is occurring in this system.

Sparge Gas

Experiments have shown that the gas within the bubble can dramatically effect the cavitation conditions. Monatomic gases produce higher temperatures during bubble collapse because less energy is lost through translational degrees of motion. Gas with a low thermal conductivity prevents loss of heat to the surrounding medium, which also increases the internal bubble temperature. Noble gases such as argon or xenon possess both of these characteristics and work well to maximize the extreme conditions of cavitation, while air is known to dilute the effects (Price 1992).

A sample of actual NC fines was cooled to 5 °C and sonicated at 20 kHz for 1-hour and 5-hour times using either air or argon as a sparge gas. Figures 14a through 14d show the LC chromatograms for these four conditions. Figures 14a and 14b show very little difference in the production of the sonolysis by-product at 2.4 minutes with argon as a sparge gas for either 1 or 5 hours of sonication. Use of air as the sparge gas is surprisingly similar, as seen in Figures 14c and 14d with a small increase in the by-product peak abundance between 1 and 5 hours. It may be that the fine colloidal suspension of NC fines in this sample provides good nucleation sites for cavitation, regardless of the entrained gas.

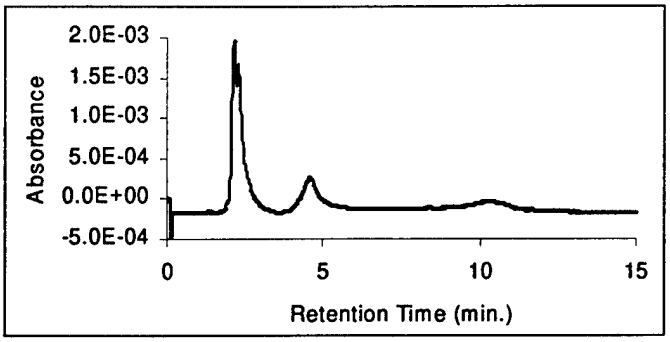

Figure 14a. LC of actual NC fines after sonication for 1 hour using argon as the sparge gas.

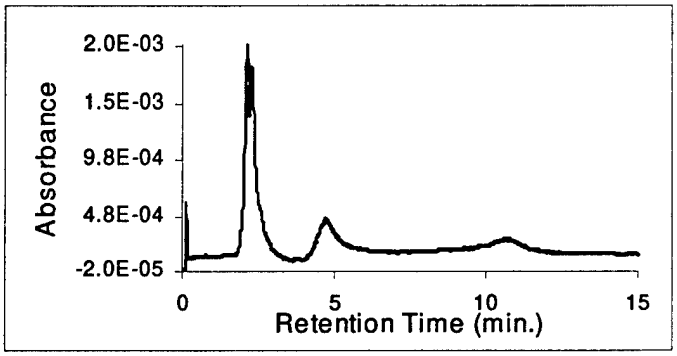

Figure 14b. LC of actual NC fines after sonication for 5 hours using argon as the sparge gas.

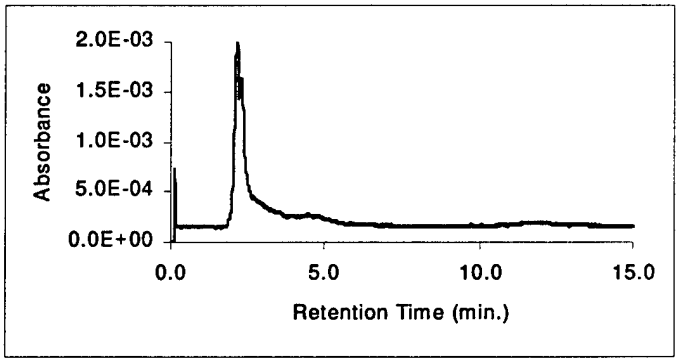

Figure 14c. LC of actual NC fines after sonication for 1 hour using air as the sparge gas.

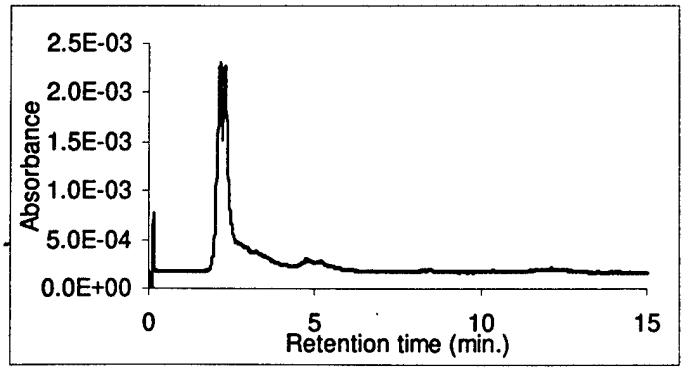

Figure 14d. LC of actual NC fines after sonication for 5 hours using air as the sparge gas.

The simulated NC sample was also sonolyzed using the same experimental conditions. Figure 15 shows the resulting four LCs. With argon as the sparge gas, the 1-hour run shows a large amount of the by-product (Figure 15a). After 5 hours (Figure 15b), however, the by-product concentration has decreased by a factor of four. It is likely that the solution has degassed sufficiently over the 5 hours, significantly reducing the cavitation events, decreasing the by-product production, and possibly degrading the by-product as well. Interestingly, concomitant with the by-product decrease is an increase in the unretained peak at 2.0 minutes, which has a retention behavior similar to the nitrate/ nitrite peaks seen earlier (Figure 3). This increase may indicate that the sonolytic by-product contains a nitrogen oxide substituent that is cleaved during its degradation. Figures 15c and 15d show the results using only entrained air in the sample. Only a small increase is noted in the absorbance after the injection peak in the 5-hour run. Very little sonolytic by-product, if any, is produced with air as a sparge gas. The large agglomerations of the 11.5% nitrated NC are not as well dispersed as a colloidal suspension and thus provide fewer nucleation sites in the active regions of the vessel. When compared to the actual NC fines with air as the entrained gas (Figures 14c and 14d), it is apparent that the simulated NC fines solution is easily degassed.

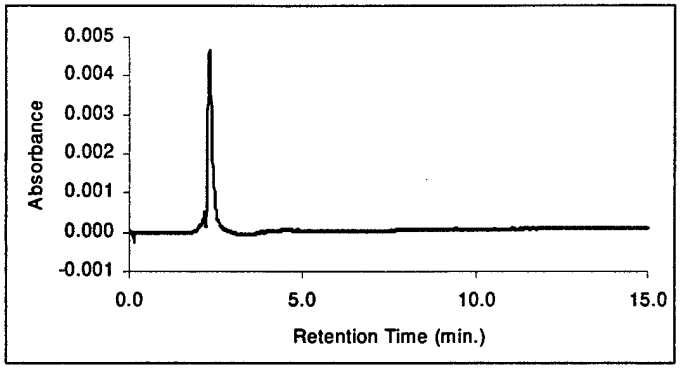

Figure 15a. LC of simulated NC fines after sonication for 1 hour using argon as the sparge gas.

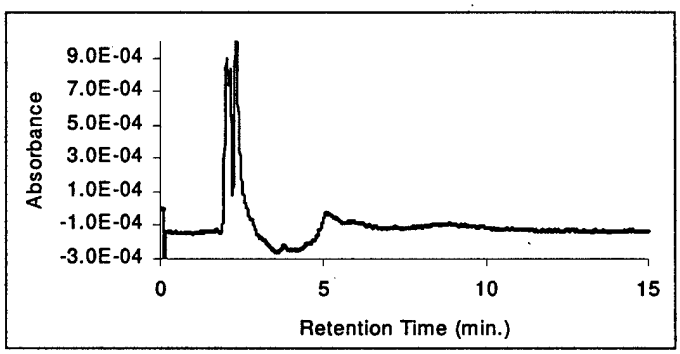

Figure 15b. LC of simulated NC fines after sonication for 5 hours using argon as the sparge gas.

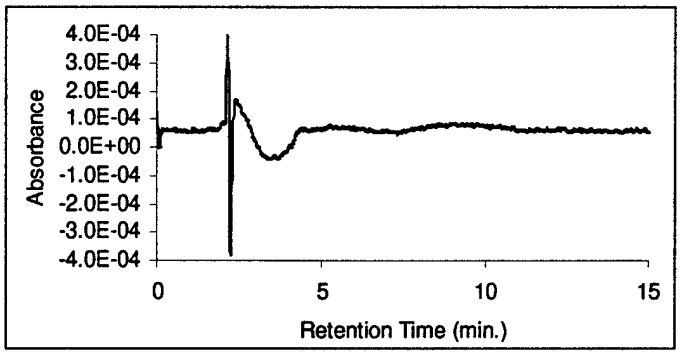

Figure 15c. LC of simulated NC fines after sonication for 1 hour using air as the sparge gas.

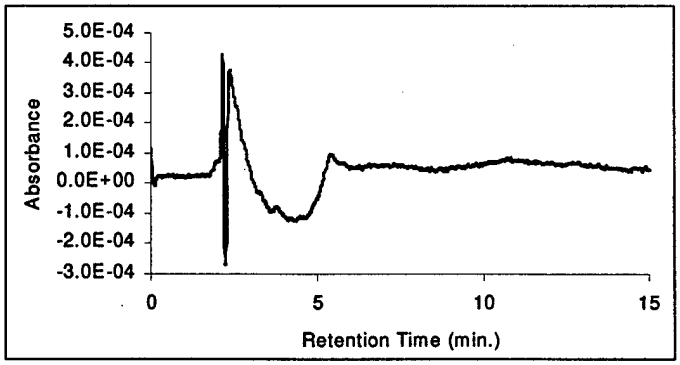

Figure 15d. LC of simulated NC fines after sonication for 5 hours using air as the sparge gas.

CE experiments were done on the simulated NC fines samples after sonication. Figure 16 is the CE of the 5-hour insonation time with air sparge. A small nitrate peak is observed in this sample due to denitration of the NC.

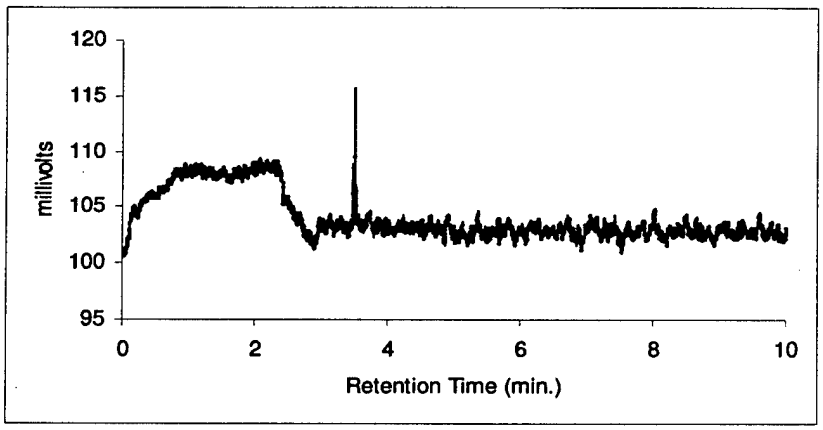

Figure 16. CE of simulated NC fines wastewater after sonication for 5 hours using air as the sparge gas.

Solvent Effects

Degradation is more extensive when the polymer is extended in a rod shaped configuration because more of the backbone is exposed. This configuration occurs when a good solvent is used to relax the polymer. When a poor solvent is used, the polymer adopts a ball configuration, protecting itself from degradation (Price 1990). Better degradation of NC is therefore expected in acetone, a good solvent for NC, versus water, a poor solvent.

An initial study was done to sonicate acetone for 1 hour at 20 kHz, sparging with argon and cooling to 5 °C to determine sonochemical effects on acetone alone. This solution was directly analyzed by GC/MS. Figure 17a shows that one dominant peak arises from this reaction at 5.6 minutes. This by-product is 4-hydroxy-4-methyl-2-pentanone. A sample of 11.5% nitrated NC dissolved in acetone was also sonicated under the same conditions. Analysis of this sample is provided in Figure 17b. The results show that acetone again produces this single by-product with no extractable breakdown products from the NC. An LC chromatogram of the solution (not shown) shows only the acetone peak. In this situation, dissolution into a better solvent (acetone) prevents the production of the sonolytic by-product from NC whereas a poor solvent (water) allows the degradation to occur.

A pyrogram of the NC sonolyzed with acetone as solvent has the same peaks as the original pyrogram (Figure 8) including all nitrogen-containing pyrolysis

products. This result indicates no denitration of the NC due to sonolysis. GPC analysis of this sonolyzed NC gave a molecular weight value of 93560, an increase from the original molecular weight value for 11.5% nitrated NC. Again, these sonolysis conditions are proving conducive to polymerization rather than depolymerization.

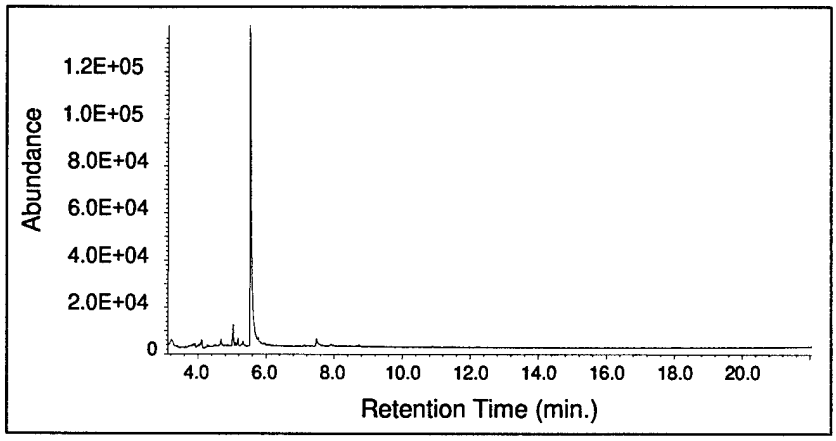

Figure 17a. GC/MS of acetone after sonication for 1 hour at 20 kHz.

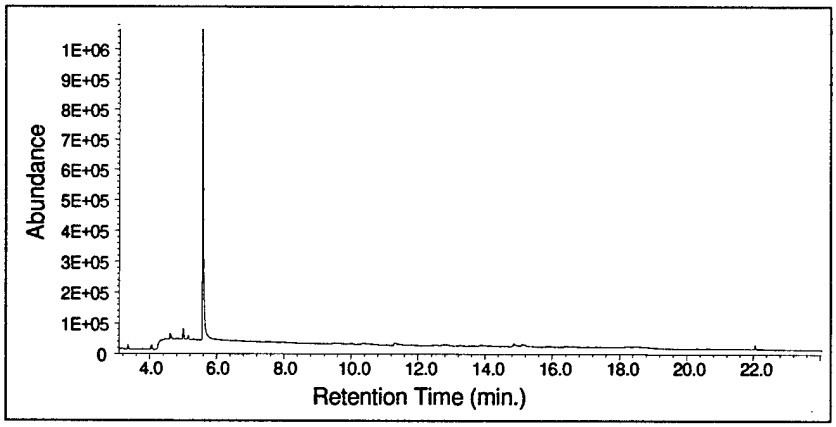

Figure 17b. GC/MS of 11.5%N NC dissolved in acetone and sonicated for 1 hour at 20 kHz.

Temperature Dependence

Previous studies have indicated that depolymerization is slower at higher temperatures (Price 1990). While all previous experiments were done using a solution temperature of 5 °C, one sonolysis of actual NC fines was done at 35 °C to note any temperature effects. Figure 18 shows the LC chromatogram of the filtered solution. The same behavior is noted as in the cooled solutions. The NC degradation product is the only observed sonolytic effect. No by-products are seen in a methylene chloride extraction and analysis by GC/MS.

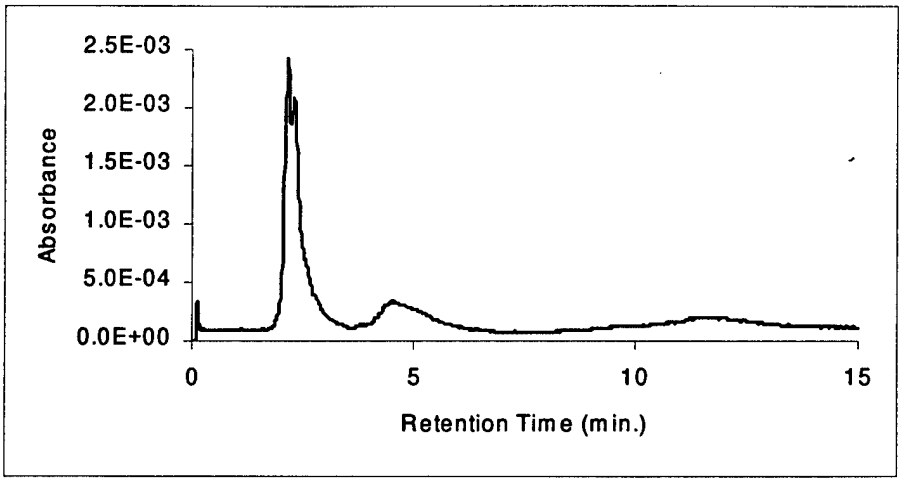

Figure 18. LC of actual NC fines after sonication for 1 hour at 20 kHz, solution maintained at 35 °C.

5 Conclusions

As discussed in Chapter 4, the dominant effect of sonolysis on macromolecules is depolymerization until a limiting Mw is reached. GPC results have shown in this work that sonolysis of NC produces instead an Mw increase. This effect has been noted when the initial Mw of the macromolecule is below the depolymerization Mw limit. Polymerization to the Mw limit is then the primary behavior of the system. It appears that the NC fines Mw is below the limit and slow polymerization is occurring.

LC data showed the slow production of a single sonolytic by-product originating from the NC. This by-product was never identified. CE data indicated that very slight denitration did occur only after long sonolysis times; therefore, the energetic properties of the NC are likely unaffected unless sonolyzed for impractically long periods. Pyrolysis data on the solid NC after sonolysis provided no evidence of molecular alterations. GC/MS results showed no production of organic fragments.

Based on the lack of extensive degradation of NC, even after 5 hours of irradiation, sonolysis of NC is unlikely to find a niche as an innovative NC fines treatment method unless further breakthroughs are found to increase the degradation kinetics.

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Nitrocellulose (NC) fines are the small polymer fibers of NC that are not separable from the NC production stream by settling or centrifugation. Wastewater containing NC fines at a concentration of 150 to 400 parts per million is one of the largest volume waste streams produced by the Army. Current methods of control and disposal depend upon the lack of strict regulations regarding the environmental release of NC fines. Possible changes in the interpretation of state regulations would create immediate disposal problems. Numerous research efforts have investigated NC treatment methods from the novel to the mundane. This report provides data on the effects of high intensity ultrasound on NC degradation in water. The results indicate that NC is resistant to depolymerization and denitration by sonolytic means.

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