DEVELOPMENT OF A NOVEL ENVIRONMENTALLY FRIENDLY STARCH-BASED AIRCRAFT DEICER

By

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DEVELOPMENT OF A NOVEL ENVIRONMENTALLY

FRIENDLY STARCH-BASED AIRCRAFT DEICER

Abstract

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Aircraft deicing currently relies upon glycol-based deicers which exert significant biochemical oxygen demand and toxicity to receiving waters. A product derived from oxidized corn and potato starch was investigated as an alternative to glycol-based deicers. Freezing point depression ranged from 19.7 to 28 ˚C and viscosities similar to those of commercially available deicing products were obtained when oxidized starch formulations were post-treated with granular activated carbon. The product exhibited a five day biological oxygen demand between 20% and 50% that of glycol-based deicers. However, the LC_{50} to *Ceriodaphnia dubia* was 2.73 g/L which is greater than glycol-based deicers (18.3 g/L for propylene glycol and 34.4 g/L for ethylene glycol). Corrosion testing indicated compatibility with aerospace materials in most cases. Organic acids were identified by gas chromatography/mass spectrometry as the primary constituents in the pretreated starch solution and their sodium salts are likely responsible for freezing point depression. The results represent an important step towards development of more environmentally benign deicing products.

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INTRODUCTION

Aircraft deicing is necessary for flight operations in adverse weather conditions to prevent the accumulation of ice or remove ice that may have formed on aircraft wings and control surfaces. Ethylene glycol and propylene glycol are currently the most commonly used aircraft deicers. These synthetic chemicals often have detrimental effects on the environment (Corsi et al., 2006). Ethylene glycol exerts a theoretical oxygen demand (ThOD) of 1.11 g O_2/g, and the ThOD of propylene glycol is 1.68 g O_2/g. However, advantages of propylene glycol include greater freezing point depression (Castro et al., 2005) and lower aquatic toxicity than ethylene glycol. Commercially available fluids are often a blend of both glycols. Furthermore, production of ethylene and propylene glycol often relies upon petroleum-derived propylene and ethylene. Therefore, selection of an anti-icing fluid requires balancing deicer effectiveness with environmental concerns. New deicers are needed to minimize environmental effects and provide a sustainable and economically competitive alternative to ethylene and propylene glycols.

Oxidation of vegetable starch has provided a carbon source for numerous industrial and production applications. For example, oxidative modification of starch has been used in the paper coating industry as a method for reducing the viscosity of starch suspensions (Parovuori et al., 1995). Oxidized starches have also been used as food additives and as a complexing agent in detergents (Mathew and Adlercreutz, 2009). Modified Fenton's reagent is a process that can provide efficient production of reactive oxygen species. The standard Fenton initiation reaction is the iron (II) catalyzed decomposition

of hydrogen peroxide (H_2O_2) at acidic pH, which produces hydroxyl radical ($OH\cdot$) in near-stoichiometric yield (Walling, 1975):

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH\cdot + OH^- \qquad (1)$$

The standard Fenton's reaction is often modified to generate a series of reactive species or to allow the reaction to proceed under various conditions. When iron (III) catalyzes the decomposition of H_2O_2, production of superoxide ($O_2\cdot^-$) is favored and the reaction proceeds through an alternate initiation reaction:

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + HO_2\cdot + H^+ \qquad (2)$$

Furthermore, when H_2O_2 is added in excess of stoichiometric requirements, propagation reactions are promoted resulting in the generation of perhydroxyl radical ($HO_2\cdot$), superoxide radical anion ($O_2\cdot^-$), and hydroperoxide anion (HO_2^-):

$$OH\cdot + H_2O_2 \rightarrow HO_2\cdot + H_2O \qquad (3)$$

$$HO_2\cdot \leftrightarrow O_2\cdot^- + H^+ \qquad (4)$$

$$HO_2\cdot + O_2\cdot^- \rightarrow HO_2^- + O_2 \qquad (5)$$

The reactive oxygen species generated from the modification of Fenton's reactions have been successfully employed to transform recalcitrant organic compounds in contaminated soil and groundwater (Teel and Watts, 2002). However, the process has recently been applied in a number of other applications including chemical oxygen demand (COD) removal in industrial wastewater and the pretreatment of drinking water prior to chlorination (Murray and Parsons, 2004; Badawy and Ali, 2006).

Freezing point depression in aqueous solutions composed of modified monomeric organic molecules has recently been studied. Yang and Montgomery (2003) reported freezing point depressions up to 28°C for solutions containing the sodium salts of sugar acids obtained by alkaline hydrolysis of glucose and subsequent neutralization with sodium hydroxide (NaOH). Similarly, Ganjyal et al. (2007) observed freezing point depression of 15°C for a 40 percent solution of sodium levulinate produced by neutralization of grain sorghum hydrozylate. In each case, the organic acids created through hydrolysis are countered with a monovalent alkali metal hydroxide to form organic salts, increasing the ionic strength of the solution and depressing the freezing point. While it is not clear what mechanism is responsible for the oxidative modification of starch by Fenton's reagent, hydrolytic cleavage of glycosidic bonds, followed by subsequent oxidation of the monomer and oligomer products is one likely mechanism.

The objective of this research was to evaluate corn and potato starch oxidized by modified Fenton's reagent for use in aircraft deicing and anti-icing. The parameters assessed include physical properties (freezing point depression and viscosity) and environmental impacts (chemical and biological oxygen demand). Starches are a common constituent in food processing wastes and have the potential to provide an alternative feedstock for deicer and anti-icer production. If modified starch solutions are viable deicing agents, benefits would include potential cost savings while promoting sustainability through beneficial use of a waste product.

EXPERIMENTAL

Materials

Chloroform, sodium hydroxide (NaOH), sulfuric acid (H_2SO_4), iron(III) EDTA, and pyridine were purchased from JT Baker (Phillipsburg, NJ). Corn starch was obtained from ACH Foods (Memphis, TN) and potato starch was purchased from EM Science (Gibbstown, NJ). Hydrogen peroxide (50% w/w), bis(trimethyl)triflouroacetamide (BSTFA) and DARCO activated carbon were purchased from Sigma Aldrich (St. Louis, MO). F-200 and F-300 activated carbon were provided *gratis* by Calgon Carbon (Pittsburgh, PA). Seed microorganisms for Biological Oxygen Demand (BOD) were obtained from Polyseed (The Woodlands, TX). Reagents for nitrate measurement were purchased from Hach (Loveland, CO). Linear alkyl benzene sulfonate stock solution was purchased from Ricca Chemical Company (Arlington, TX). Dialysis tubing was purchased from Spectrapore (Rancho Dominguez, CA). Metal coupons of a given alloy were taken from a single stock sheet and finished per ASTM standards by Metal Finishing Company (Wichita, KS). All reagent water (>17 MΩ·cm) was from a Barnstead Nanopure II ultrapure system.

Evaluation of pretreated starch solutions for aircraft deicing followed four specific steps:

1. Evaluation of the substrate and oxidant dose that provided the greatest freezing point depression,
2. Optimization of the oxidation pretreatment procedure,
3. Optimization of post-treatment procedure, and

4. Determination of the chemical and biochemical oxygen demand and toxicity of the pretreated starch solution.

Initial Evaluation of Substrates and Oxidant Dose

A central composite rotatable design (CCRD) using 13 trials and 5 center points was used to determine the effect of starch to oxidant (H_2O_2) ratios on the freezing point depression properties of the oxidized starch solution. CCRD designs have an advantage over factorial designs in that fewer trials are needed to obtain data of similar accuracy (Diamond, 1989). CCRD analysis was performed with both corn starch and potato starch with the substrate:oxidant ratios listed in Table 1. The coded values are scaling factors common to all CCRD experiments while the real values are the actual masses of starch and volumes of H_2O_2 used. Trials 1 through 8 quantified freezing point response across the range of test values while trials 9 through 13 were replicates (center points) used to assess precision. Reactions were conducted in 1 L Erlenmeyer flasks with agitation on a shaker table at 175 rpm until all of the hydrogen peroxide was consumed. The liquid phase (water and H_2O_2) was held constant at 100 mL and 0.18 g iron (III)-EDTA was added to provide a 5 mM liquid phase iron concentration.

Table 1 Central composite rotatable design matrix parameters for determination of freezing point depression.

	Coded		Real	
Trial	**Starch Mass (g)**	**[H_2O_2] (% vol.)**	**Starch Mass (g)**	**[H_2O_2] (% vol.)**
1	-1	-1	11.6	17.2
2	1	-1	43.4	17.2
3	-1	1	11.6	27.8
4	1	1	43.4	27.8
5	1.4142	0	5.0	22.5
6	1.4142	0	50.0	22.5
7	0	1.4142	27.5	15.0
8	0	1.4142	27.5	30.0
9	0	0	27.5	22.5
10	0	0	27.5	22.5
11	0	0	27.5	22.5
12	0	0	27.5	22.5
13	0	0	27.5	22.5

Chemical Oxidation Pretreatment

Based on the freezing point response surface plot (Figure 1), a hydrogen peroxide concentration of 25% and a starch mass of 50 g/100 mL hydrogen peroxide solution was selected for further evaluation (This ratio was selected because it provided near optimum freezing point depression with minimal oxidant use). Pretreated starch solutions were prepared in batches containing 100 g starch and 200 mL 25% (vol/vol) hydrogen peroxide in 2 L Erlenmeyer flasks. Iron (III)-EDTA (0.37 g) was added prior to H_2O_2 addition to provide a concentration of 5 mM. The reactions proceeded for 24 h with agitation at 175 rpm. After 24 hr, the flasks were dosed with 12.5 mL of 12M sodium hydroxide (NaOH) to ensure complete decomposition of the hydrogen peroxide, and allowed the reaction to proceed to completion. After the reaction was complete, the

samples were adjusted to pH 7.5 by addition of NaOH. To increase freezing point depression, samples were concentrated by placing in an oven at 55˚C and evaporated until a final volume equal to 120 mL/100 g of starch treated was achieved.

Pretreated Starch Post-Treatment

Two post treatments were evaluated to reduce the viscosity of the pretreated starch solutions through selective removal of higher molecular weight oxidation products. Post treatment was evaluated through treatment (1) with granular activated carbon (GAC) and (2) by diffusion through dialysis tubing.

Post treatment with GAC was conducted by adding GAC to a 120 mL aliquot of the test solution in a 1 liter Erlenmeyer flask. The flask was agitated on a shaker table at 175 rpm for 48 hr. After removal from the shaker table, the slurry was passed through a screen under vacuum to provide coarse particle separation. Finer particles were removed by centrifugation at 4000 rpm for 10 min. The supernatant was decanted and readjusted to pH 7.5 prior to viscosity and freezing point determination.

Dialysis post treatment was performed by suspending cellulose ester dialysis tubing (molecular weight cutoff of 500 Daltons) in approximately 19 L of continuously mixed deionized water. Dialysis proceeded for 168 hr followed by evaporation of the dialysate to 120 mL. The evaporated dialysate was adjusted to pH 7.5 prior to freezing point determination.

Freezing Point Determination

The freezing point of all oxidized starch solutions was determined using ASTM Method D 1177. Each sample was immersed in a cooling bath prepared by adding dry ice to acetone in a 2 L Dewar flask. The freezing tube used was obtained from Lab Glass (Kingsport, TN) with dimensions of 260 mm by 54 mm outside diameter, and a volume of approximately 200 mL. Agitation was provided by a 1.6 mm diameter stainless steel rod formed into five coils at its end with a diameter such that coils touched the wall of the freezing tube. The stirrer was reciprocated by a windshield wiper motor connected through mechanical linkages (a photograph of the test apparatus is included in Appendix A). Temperature of the test solutions was monitored with a 100Ω calibrated platinum resistance thermometer (Omega Engineering, Stamford, CT) connected through an Omega Model HH804U digital temperature indicator to a Dell Inspiron 5500 computer. The output from the probe was plotted as a function of time at one sec intervals. Freezing point was determined from the slope changes on the temperature vs. time curves by determination of the temperature peak following release of the heat of fusion from the test solution.

An aliquot of pretreated starch solution was placed in the sample tube and immersed in the cooling bath such that the sample level in the freezing tube was below the bath level. A minimum sample volume of 50 mL was used to ensure adequate agitation by the mechanical stirrer and immersion of the resistance thermometer. When the temperature of the sample approached the expected freezing point, a wire loop containing a frozen droplet of deionized water was inserted to the bottom of the freezing

tube to initiate freezing with minimal sub-cooling of the bulk solution. The increase in temperature preceding crystallization of the bulk solution was usually less than 1˚C.

Viscosity Determination

Viscosity determination was performed using Oswald viscometer tubes at a constant temperature of 0˚C by suspension of the viscometer tubes in an ice water bath. The viscometer tubes were filled with the test solution and placed in the ice water bath for 10 min before measuring the viscosity to ensure that the solution was in temperature equilibrium.

Foaming Properties

The deicer solution was assayed for the presence of surfactants that may cause foaming using ASTM D 2330 (2008). A standard curve was prepared using a linear alkyl benzene sulfonate (LAS) stock solution. Preliminary pH measurement was performed conductively rather than colorimetrically (as specified in ASTM D 2330) due to the opacity of the starch solution. A 100 mL aliquot of the solution was adjusted to pH 8.2 in a 250 mL separatory funnel followed by addition of 25 mL concentrated methylene blue. Chloroform (25mL) was then added and the contents vigorously shaken for 30 sec. The chloroform layer formed at the bottom of the separatory funnel was then drained to another 250 mL separatory funnel. Two additional 25 mL chloroform extractions were conducted. Following the third chloroform extraction, phosphate buffer (prepared per ASTM D 2330) was added to the second separatory funnel and the contents mixed for an additional 30 sec. The chloroform layer was

drawn out of the funnel through a fiberglass mat into a 100 mL volumetric flask. Sufficient chloroform was added to increase the volume to 100 mL. The absorbance of the resulting solution was then measured at 650 nm on a Spectronic 20 Genesys spectrophotometer.

Chemical and Biochemical Oxygen Demand

COD was measured using Standard Method 5220 B (2005). A glucose standard curve was prepared with standards of 20, 100, 300, 600, and 900 mg/L as O_2. Each sample was digested with acidic dichromate reagent and refluxed at 103˚C for 2 hr. Sample absorbance was measured on a Spectronic 20 Genesys spectrophotometer at 600 nm. BOD at 5 days (BOD_5) and ultimate BOD (BOD_U) were determined for the pretreated starch solution using Standard Methods 5210 (2005). To determine the 5-day BOD, three dilutions of the pretreated starch solution were prepared in triplicate 300 mL BOD bottles. Each sample was seeded with microorganisms. The samples were then incubated for 5 d at 20˚C and dissolved oxygen (DO) was measured using an YSI model 52 DO meter before and after incubation.

BOD_U was computed from triplicate samples of diluted pretreated starch solution and duplicate dilution water controls. Samples were incubated in 300 mL BOD bottles at 20 ˚C and dissolved oxygen was monitored every 5 days for 60 days. Samples were reaerated as the DO approached 2 mg/L. To correct for nitrogenous oxygen demand, nitrate was measured colorimetrically at each 5-day monitoring period. BOD_U and the first order decay rate (k) were calculated based on the DO concentration vs. time assuming first order kinetics:

$$BOD(t) = BOD_U(1-e^{-kt}) \quad (8)$$

Toxicity Testing

Toxicity testing was conducted on *Ceriodaphnia dubia* using Standard Method 8712 (2005) with a GAC post-treated starch solution (50 g Calgon F-200 GAC per 120 mL).

Corrosion Testing

Corrosion testing was conducted based on ASTM standards on a number of aerospace materials prepared as coupons including aluminum alloys, titanium alloy, and coated steel. Each set of test coupons were cut from the same piece of stock using an abrasive water jet. In each case, test coupons were prepared and treated with pretreated starch solution as prescribed in the applicable ASTM standards.

Assessment of corrosive effects under conditions of total immersion was evaluated using ASTM standard F 483 (2008). The evaluation included both evaluations of mass change as well as visual changes to the test coupons resulting from treatment with the pretreated starch solution. Prior to treatment, the specimens were weighed and visually inspected. The starch solution was heated to 38˚C in a water bath for the duration of the immersion test. Following immersion of the test coupon in the pretreated starch solution for periods of 24 and 168 hours, the coupons were weighed and inspected for dulling, etching, accretions, and pitting.

Assessment of corrosive effects to unpainted aircraft surfaces were evaluated using ASTM F 485 (2008). Specimens of clad aluminum and titanium alloy were treated by

immersion with the post-treated starch solution so that approximately 50% of the coupon area was covered. Following a 30 min drying period at 45˚to the horizontal in a mechanical convection oven at 150 ˚C, the coupons were allowed to cool to room temperature and rinsed under tap water for 1 min. The coupons were then rinsed for 15 sec under deionized water and allowed to air dry for 30 min before examination of the panels for residues or stains.

Assessment of damaging effects to coated aircraft surfaces was evaluated using ASTM Standard F 502 (2008). Clad 7075-T6 aluminum test coupons were coated with a chemical conversion coating conforming to MIL-DTL-81706, Class 1A and given an epoxy polyamide primer coating (thickness equal to 0.6 to 0.8 mil) conforming to MIL-PRF-23377. A top coat (thickness equal to1.2 to 1.8 mil) conforming to MIL-PRF-85285 was applied subsequently. Pretreated starch solution was applied to approximately 50% of the panel area and the panel was placed in an oven at 38˚C for 30 min. The coupons were subsequently rinsed with deionized water, and allowed to air dry for 24 hr. The coupons were visually inspected prior to determination of coating durability (hardness). Coating hardness was determined by pushing drawing pencils (hardness equal to 6B, 5B, 4B, 3B, 2B, B, HB, F, H, 2H 4H, 5H, and 6H) of increasing hardness at an angle of 45˚ to the horizontal along treated and untreated areas of the coupon with uniform pressure until a pencil was found that cut through the coating. Prior to each hardness determination, the pencil lead was squared by abrading with 320 grit sandpaper. Coating hardness is characterized by the pencil that left a black mark but did not cut the coating, but with the next hardest pencil cutting the coating.

Assessment of corrosive effects to faying surfaces was evaluated using ASTM Method F 1110 (2008). Coupon sandwiches consisting of eight layers of 50 mm by 100 mm by 1 mm clad and anodized 2024-T3 and 7075-T6 aluminum coupons (anodized according to MIL-A-8625-Type 1 with a hot water seal) were constructed. Each sandwich consisted of one pair of coupons of each alloy separated by filter paper saturated with the test solution. A separate quadruplicate set of sandwiches was prepared and treated with deionized water to provide controls. Following the exposure regime outlined in ASTM Method F 1110, the panels were given visual inspection according to the following qualitative rating system:

0 – No visible corrosion and no discoloration present

1 – Very slight corrosion or discoloration and/or up to 5% of area corroded

2 – Discoloration and/or up to 10% of area corroded

3 – Discoloration and/or up to 25% of area corroded

4 – Discoloration and/or more than 25% of area corroded, and/or pitting present

Assessment of corrosive effects to cadmium plated surfaces was evaluated using ASTM Method F1111 (2008). Test coupons with dimensions of 25.4 mm by 50.8 mm by 1.27 mm were prepared from 4130 steel and cadmium plated to a thickness of 0.013 mm. Coupons were treated in a similar fashion to total immersion testing. Initially coupons were immersed in methyl n-propyl ketone, the excess solvent was removed, and the coupons allowed to dry in an oven at 110˚C for 1 hr. Following removal from the oven, the coupons were placed in a dessicator for 1 hr and then weighed. The coupons were then placed in the starch solution maintained at 38˚C in a water bath for

the duration of the test. After exposure for 24 hr, the coupons were removed with forceps and rinsed in a 1 L jar with constant flow of clean tap water. Following this immersion, the coupons were sequentially rinsed with deionized water and acetone and placed in an oven at 110˚C for 1 hr and cooled to ambient temperature in a dessicator. The coupons were weighed and inspected for dulling, etching, accretions, and pitting.

Qualitative Chemical Analysis

To determine the products of the oxidized starch solution, chemical analysis was conducted using gas chromatography/mass spectrometry (GC/MS). Samples were silyated using bis(trimethyl)triflouroacetamide (BSTFA) with 1% trimethyl-chorosilane (vol/vol) in pyridine as described by Bartolozzi et al. (1996). Samples of the post treated starch solution were dried at 105 ˚C and 10 mg of the resulting material weighed out and added to a 2 mL target vial. 1 mL of pyridine and 400 µL of BSTFA were added, and the vial was capped. The vial was mixed on a vortex mixer for 1 min before placing the vial in an oven at 60 ˚C. After 2 hr, the vial was removed and mixed on a vortex mixer for 1 min. All suspended particles were allowed to settle prior to removing the supernatant. The extracted liquid was then discharged into another target vial and analyzed by gas chromatography on an HP 5890 Series II gas chromatograph with a Supelco (St. Louis, MO) SPB-5 (15 m x 0.53 mm x 1.5 µm) column and flame ionization detector (FID) to determine an appropriate temperature program.

Using the temperature program developed on the GC/FID to provide adequate resolution and peak separation, the samples were analyzed using an Agilent 7890A GC with an Agilent (Santa Clara, CA) HP-5HS (30 m x 0.250 mm x .25 µm) column coupled

with a 5975C mass selective detector to determine specific chemical constituency. Compound identification was made by referencing the mass spectrum associated with major peaks on a plot of total ion current (TIC) to the National Institute of Standards and Technology (NIST) mass spectra library.

RESULTS AND DISCUSSION

Initial Evaluation of Substrates and Oxidant Dose

A response surface plot showing freezing temperature at various corn starch and hydrogen peroxide doses is shown in Figure 1. A comparison of freezing point depression data for corn starch and potato starch is shown in Table 2. Due to incomplete dissolution of oxidation products, a freezing point response surface plot was not constructed for potato starch. Initial evaluation of freezing point depression indicated that oxidized corn starch promoted greater freezing point depression than potato starch over the range of oxidation conditions evaluated. Maximum freezing point depression of 12°C was observed with 50 g starch/100 mL and 22.5% hydrogen peroxide. Based on the response surface plot for corn starch (Figure 1), oxidation conditions of 50 g starch per 100 mL oxidant solution and 25% hydrogen peroxide were selected for post-treatment evaluation. These conditions were chosen because they provided near optimum freezing point depression while providing a practical mass of starch and volume of hydrogen peroxide if the process is scaled to a larger level.

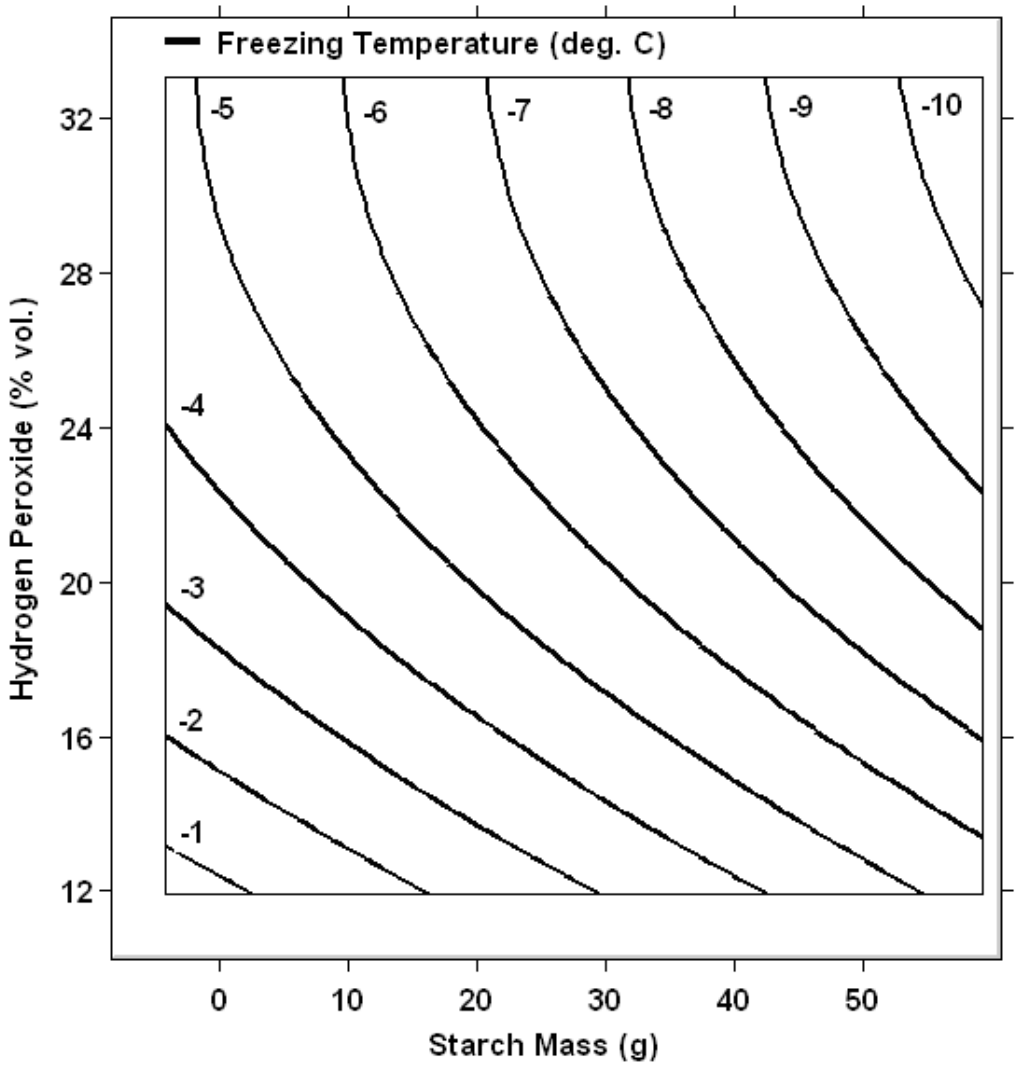

Figure 1 Response surface plot of oxidized corn starch solution freezing temperature as a function of hydrogen peroxide concentration and starch mass.

Table 2 Comparison of freezing point for solutions of oxidized potato and corn starch (not treated with NaOH) at ratios of starch to H_2O_2 listed in Table 1.

Sample #	Initial Starch Mass (g)	Potato Starch Freezing Point (˚C)	Corn Starch Freezing Point (˚C)	Difference (˚C)
1	11.6	-2	-3.7	1.7
2	43.4	NA*	-9.6	NA
3	11.6	-2.5	-3.5	1
4	43.4	-7.8	-10.6	2.8
5	5	-2.2	-1.9	0.3
6	50	NA*	-12.6	NA
7	27.5	NA*	-7.3	NA
8	27.5	-5	-7.5	2.5
9	27.5	-4.7	-7.3	2.6
10	27.5	-4.4	-7.5	3.1
11	27.5	-4.8	-7.4	2.6
12	27.5	-4.6	-7.3	2.7
13	27.5	-4.7	-7.6	2.9

* Potato starch did not completely dissolve.

Concentration and Post-treatment of Oxidized Starch Solutions

Oxidized starch solution properties with different post-treatments are summarized in Table 3. A complete process diagram indicating the post treatments employed for each experimental procedure is located in Appendix A. Evaporation of the oxidized starch solutions resulted in freezing point depression up to 28˚C. However, the evaporated solutions had viscosities greater than 140 cP at 0˚C which would be difficult to apply to aircraft surfaces. High molecular weight compounds were likely responsible for the high viscosity of the oxidized starch solutions; therefore, GAC and dialysis treatment were employed to lower the viscosity. Mass loadings of 5 g, 25 g, and 50 g GAC/120 ml provided decreased viscosity with increasing GAC loading. Furthermore, freezing point increased with increasing GAC loading. These findings show that higher molecular

weight oxidation products were not only responsible for increased viscosity but also for increased freezing point depression. These results were confirmed when the freezing point was normalized to total dissolved solids (TDS) to yield the same theoretical TDS concentration as the control. In each case, depression of freezing point normalized for TDS was less for samples treated with GAC. When the sample treated with 50 g DARCO GAC was evaporated by a factor equal to the TDS concentration of the control over sample TDS, the freezing point decreased to -26.2˚C while the actual TDS concentration increased less than 2% to 543 g/L and the viscosity rose from 11 to 33 cP.

Different activated carbons were not equally effective in lowering the viscosity of oxidized starch solutions. DARCO GAC (12-20 mesh) provided the greatest viscosity reduction, followed by F-200 (12-40 mesh) and F-300 (9-30 mesh). However, the viscosity corresponding to a given freezing point was similar with all products. DARCO GAC required approximately 10% of the GAC compared to F-300 to achieve the same viscosity and freezing point (when normalized for TDS). Similarly, significantly more F-200 GAC was required to achieve the same viscosity reduction. Post-treatment with 50 g DARCO GAC provided a viscosity similar to commercially available deicers in application ready dilutions (DOW, 2009). By addition of polymers to the pretreated starch solutions, it may be possible to alter viscosity for ground and in-flight deicer application.

Table 3 Properties of oxidized starch solutions with different GAC post-treatments

Granular Activated Carbon Type	Carbon Mass (g/100 mL)	Freezing Point (˚C)	Kinematic Viscosity at 0˚C (cP)	Total Dissolved Solids (g/L)	TDS Normalized Freezing Point (˚C)*
Sigma Aldrich DARCO 12-20 Mesh	50	-19.7	11	534	-23.4
	25	-22.7	52	569	-25.3
	5	-25.8	104	585	-28.0
	0	-28.0	143	634	-28.0
Calgon F-300 9-30 Mesh	50	-26.2	100	626	-27.4
	0	-28.0	221	655	-28.0
Calgon F-200 12-40 Mesh	50	-22.8	70	557	-26.0

* The TDS normalized freezing point assumes that there is a linear relationship between TDS and freezing point. In other words, if the TDS constituency present in the solution was increased to an amount equal to the TDS of the control, the freezing point of this solution would be approximated by the TDS normalized freezing point. TDS normalized freezing point equals the observed freezing point multiplied by the ratio of TDS in the control to TDS in the sample.

Diffusion of the oxidized starch solutions through dialysis tubing also resulted in decreased viscosity in the dialysate. A normalized freezing point of -28˚C was achieved with dialysis post-treatment. However, the dialyzed sample was much more viscous, required considerably more time to prepare, and did not appear to offer an operational advantage over GAC treated samples.

Foaming Properties

Methylene blue active substances (MBAS) were found to be relatively low in the oxidized starch solution. MBAS was 150 µg/L as linear alkyl benzene sulfonate (LAS),

molecular weight = 340, which is relatively low compared to other industrial waters. Lin et. al. (1999) described the effect of LAS on foaming in domestic wastewater; MBAS concentrations >10 mg/L promote foaming. Because the measured MBAS in the oxidized starch solution was nearly two orders of magnitude less than the concentration reported by Lin et. al. (2009), foaming of the pretreated starch solutions would likely be minimal.

Chemical and Biochemical Oxygen Demand

Results of COD and BOD analysis of the GAC treated oxidized starch solutions and comparison of these solutions to the COD and BOD of glycols are listed in Table 4. The oxidized starch solution treated with 50 g of DARCO activated carbon was evaluated for chemical and biochemical oxygen demand because it exhibited a similar rheology to commercially available compounds. The COD of the oxidized starch solution was 340 g/L. COD was significantly lower for post treated oxidized starch solutions than for the glycols. Normalized to the TDS mass, the COD of the anhydrous deicer was 0.637 g O_2/g deicer. The ThOD of ethylene glycol is 1.11 g O_2/g and the ThOD of propylene glycol is1.68 g O_2/g. In summary, the COD of the pretreated starch solution is significantly lower than that of the glycols, and represents less of a threat to receiving waters than glycol-based deicers.

Biochemical oxygen demand of the GAC treated oxidized starch solution is listed in Table 5. BOD_5 was 103 g/L. BOD_U, based on BOD exerted after 60 days, was 229 g/L. Based on BOD_U of 229 g/L, the predicted BOD was computed at five day intervals using Equation 8. A summary of BOD results is listed in Table 5 and the actual and predicted

oxygen depletion as a function of time are shown in Figure 2. Because the ultimate BOD is only 67% of the COD, 33% of the oxidized starch solutions are comprised of a slowly biodegradable fraction. Although chemical composition and physical properties may vary between GAC treated solutions (solutions with higher TDS will also likely exhibit a greater proportion of higher molecular weight constituents), oxygen demand will likely vary in proportion to total dissolved solids (TDS) concentration.

Table 4 Comparison of COD and BOD for an oxidized starch solution given GAC post-treatment with ethylene glycol and propylene glycol.

Product	COD (g O_2/L)	Mass Normalized COD (g O_2/g)	BOD_5 (g O_2/L)	Mass Normalized BOD_5 (g O_2/g)
Ethylene Glycol	1230	1.11*	1000**	1110
Propylene Glycol	1860	1.68*	400 – 800**	410 - 830
GAC Treated Oxidized Starch	340	0.637	103	193

* COD was estimated as ThOD.
** BOD_5 estimates reported by Switzenbaum et. al. (2001).

Table 5 Biochemical oxygen demand for an oxidized starch solution treated with 50 grams DARCO activated carbon.

BOD_5 (g/L)	BOD_5 Standard Error	BOD_{60} (g/L)	BOD_{60} Standard Error	COD (g/L)	BOD_{60} % of COD	Oxygen depletion rate constant (1/d)
103	3.16	229	10.21	340	67%	0.097

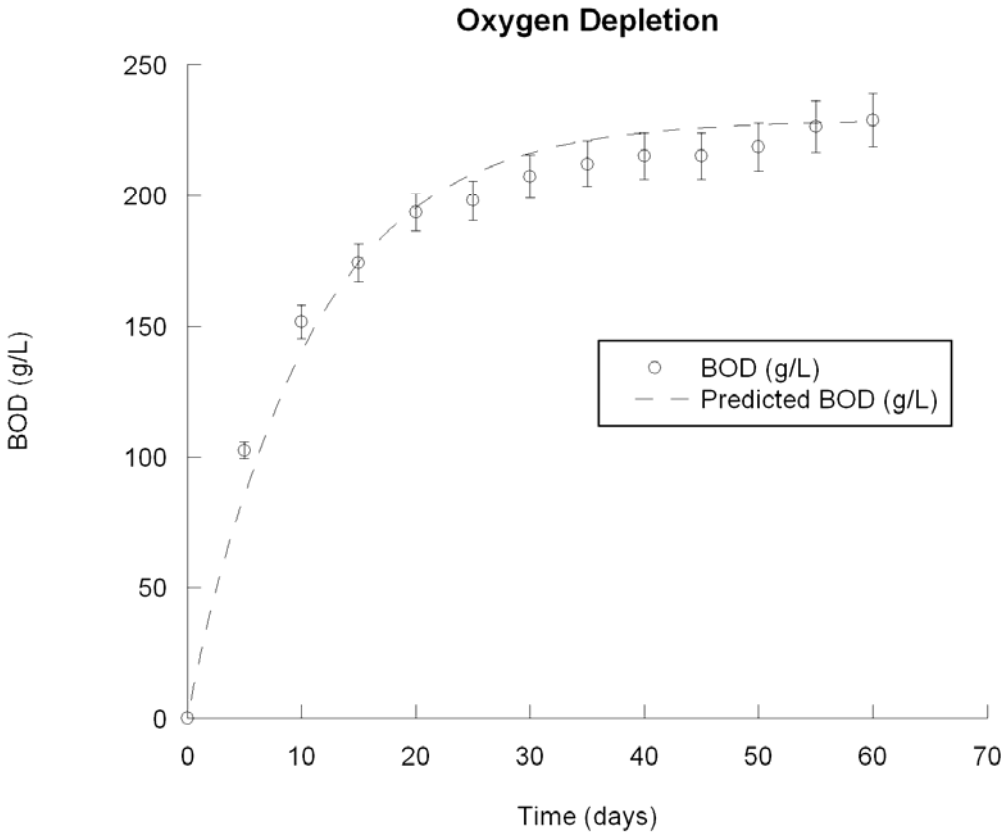

Figure 2 Observed and predicted biochemical oxygen demand with time for samples treated with 50 g DARCO activated carbon. Error bars equal the standard error of six replicates.

Toxicity Testing

A comparison of 48-hr LC_{50} to *Ceriodaphnia dubia* is listed in Table 6. The 48-hr LC_{50} to *Ceriodaphnia dubia* was 3.52 mL/L (2.73g/L) for the oxidized starch solution given post-treatment with F-200 GAC. This toxicity is greater than that of pure propylene glycol which exhibits a 48 hr LC_{50} of 18.3 g/L to *Ceriodaphnia dubia* (Pillard, 1995). Glycols formulated for aircraft deicing exhibit greater toxicity due to the presence of

corrosion inhibitors and other additives (Corsi et al., 2006). These additives may also be required in oxidized starch-based deicers. The increased toxicity of the GAC treated oxidized starch deicer may be the result of furans generated by the oxidation of monomer sugars (Perez Locas and Yaylayan, 2004). Future work may include identifying toxic compounds and the selective removal of these constituents.

Table 6 Comparison of 48-hr LC_{50} to *Ceriodaphnia dubia* for an oxidized starch solution given GAC post-treatment with both pure and deicer formulated ethylene glycol and propylene glycol.

Product	LC_{50} (g/L)
Ethylene Glycol (Pure)	34.4*
Propylene Glycol (Pure)	18.3*
Ethylene Glycol (Formulated)	13.1*
Propylene Glycol (Fromulated)	1.02*
GAC Treated Oxidized Starch	2.73

* LC_{50} reported by Pillard (1995)

Corrosion Testing

Corrosion testing results for the GAC treated oxidized starch solution is listed in Tables 7-9. The absence of visible corrosion under conditions of total immersion in conjunction with low coupon mass loss suggests that pretreated starch solutions are suitable for application to aircraft materials. Furthermore, application of pretreated starch solutions to painted and unpainted surfaces (Table 8) indicates acceptability as a deicer for aircraft exteriors. However, the sandwich corrosion test (Table 9) showed significant damage to samples, suggesting that the solutions may not be acceptable for use on exposed faying surfaces. Corrosion between faying surfaces may be the result of organic acid salts that gave the solution a strong electrolytic effect. Additionally, the

potential to corrode between faying surfaces may prove problematic if adequate sealing of faying surfaces is not done prior to deicer application. In general, corrosion testing indicated little effect of the pretreated starch solution on the aerospace substrates tested.

Table 7 Mass loss due to corrosion and qualitative comparison of samples tested in accordance with ASTM F483 and F1111.

ASTM Test Method	Alloy	Average Mass Loss ($mg/cm^2/24hrs$)		Comments
		24 hours	168 hours	
F483	7075-T6 Alclad Aluminum	0.03 ± 0.003	0.16 ± 0.016	No visible corrosion
F1111	4130 Steel (Cadmium Plated)	0.28 ± 0.016	NA	No visible corrosion

Table 8 Qualitative evaluation of unpainted and painted surfaces according to ASTM F485 and F502.

ASTM Test Method	Alloy	Results
F485	7075-T6 Alclad Aluminum	No evidence of residue or stain
	6Al-4V Titanium	No evidence of residue or stain
F502	7075-T6 Alclad Aluminum (Coated*)	Both exposed and unexposed panels were abraded at a minimum pencil hardnesss of 4H. No streaking, discoloration or blistering of the finish was evident.

Table 9 Qualitative evaluation of sandwich corrosion effects per ASTM F1110

Replicate	2024-T3 Anodized Aluminum	2024-T3 Alclad Aluminum	7075-T6 Anodized Aluminum	7075-T6 Alclad Aluminum
1	4	3	4	4
2	4	3	4	4
3	4	3	4	4
4	4	4	4	4

0 – No visible corrosion and no discoloration present.
1 – Very slight corrosion or discoloration and/or up to 5% of area corroded.
2 – Discoloration and/or up to 10% of area corroded.
3 – Discoloration and/or up to 25% of area corroded.
4 – Discoloration and/or more than 25% of area corroded, and/or pitting present.

Qualitative Chemical Analysis

A chromatogram of the post treated oxidized starch solution is shown in Figure 3, and the compounds identified in the extract with their relative proportions are listed in Table 10. These results indicate that carboxylic acids comprise the majority of the pretreated starch solutions; acetic, propanoic, and butanedioic acids are the predominant organic acid constituents. These acids may be harmful to aircraft materials and their sodium salts may contribute to an electrolytic effect, promoting corrosion of faying surfaces. Furancarboxylic acid was detected in small amounts (0.4% of total extract) and may be partially responsible for aquatic toxicity. However, sodium acetate and potassium acetate have been used as runway deicers (Switzenbaum et. al., 2001) so oxidized starch solutions may be useful as road and runway deicers.

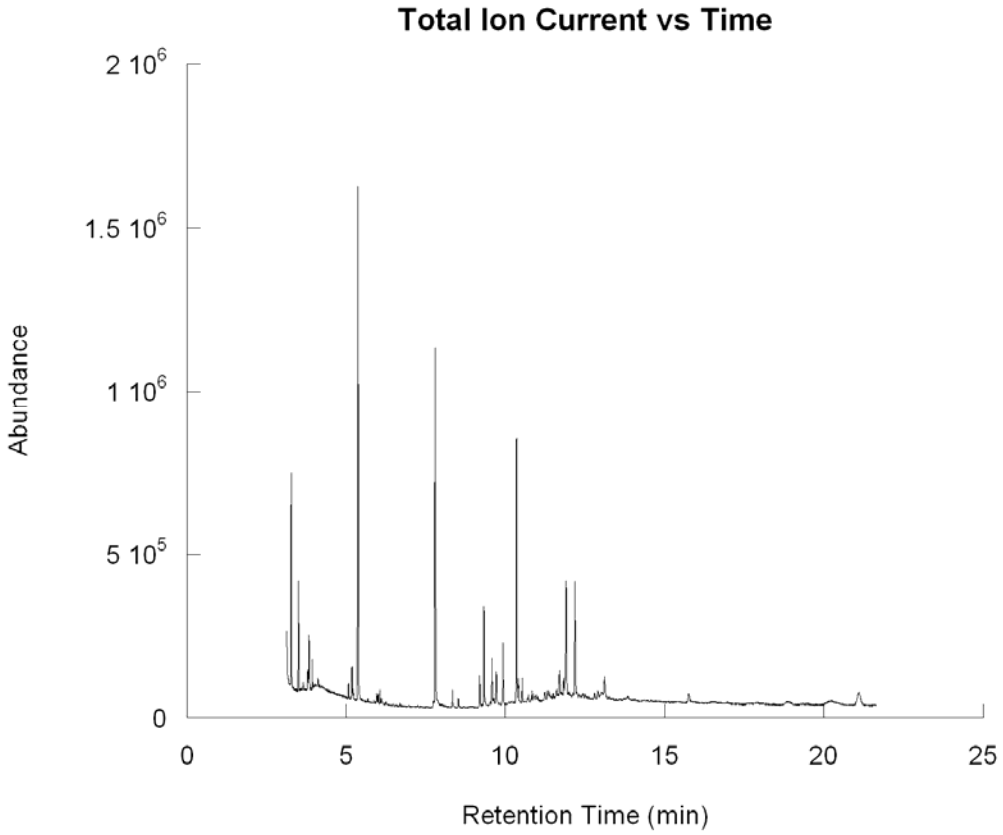

Figure 3 Total ion current as a functions of time for a sample of pretreated starch derivatized with BSTFA.

Table 10 Compound identification from GC/MS analysis for the ten most abundant constituents (excluding derivatization artifacts).

Compound Identification	Retention Time (min)	Percent of Total
Acetic acid	5.38	29.2%
Propanoic acid	7.80	21.2%
Butanedioic acid	10.35	16.3%
D-Glucopyranose	12.19	7.49%
2-Butenedioic acid	11.91	7.46%
Pentenoic acid,	9.33	4.79%
Butanedioic acid	9.93	2.59%
L-Threonic acid	9.59	1.60%
Maltose	21.11	1.44%
DL-Malic acid	9.20	0.98%

This research represents proof of concept for the use of oxidized starch solutions for deicing operations and demonstrates a potential ecological advantage. In addition, use of starch-based waste products could potentially be used as feedstock, perhaps providing an economic advantage over existing products.

CONCLUSIONS

Aqueous solutions of modified corn and potato starch were oxidized using modified Fenton's reagent as a basis for lowering the freezing point for aircraft deicing. Freezing point depression of oxidized starch solutions was as high as 28˚C, which approaches that of commercially available glycol deicers. Oxidized starch solutions were highly viscous (>140 cP), therefore, high viscosity compounds were removed with GAC post-treatment. Pretreated starch solutions exert a BOD_5 up to six times less than glycol deicers but have a 48-hr LC_{50} to *Ceriodapnia dubia* 2.5 times greater than propylene glycol. Furthermore, aircraft materials compatibility was demonstrated with the exception of application to faying surfaces using ASTM tests F483, F485, F502, F1110, and F1111. Carboxylic acids were identified as the primary constituents of oxidized starch solutions. The results of this proof of concept study demonstrate that oxidized starch solutions have benefits over glycol deicers with the exception of possible aquatic toxicity and sandwich corrosion.

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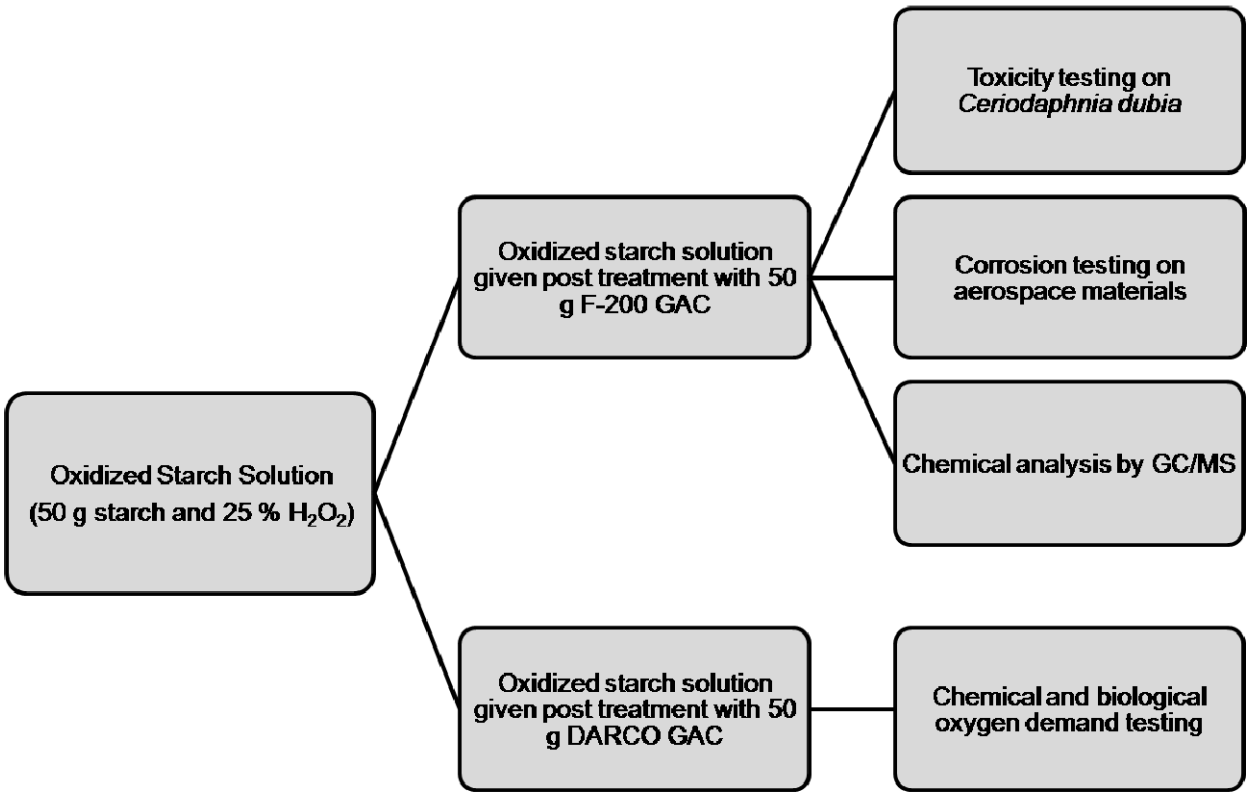
APPENDIX A: EXPERIMENTAL METHODS

Photograph of freezing point apparatus built in accordance with ASTM D 1177.



A Flow chart depicting experimental sequence