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Solid Phase Extraction (SPE) for Biodiesel Processing and Analysis

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14. ABSTRACT This report addresses evaluation of polypropylene nanofiber materials provided by Apollo NanoTech Inc. for their potential to remove glycerol and other contaminants from biodiesel preparations. This work was completed in parallel with the development of novel organosilicate sorbent materials directed at these applications. Solid phase extraction (SPE) offers the potential to reduce the volume of wastewater streams currently associated with biodiesel production. The polymer materials evaluated here are shown to remove glycerol from biodiesel preparations more effectively than commercially available SPE materials.									
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EXECUTIVE SUMMARY

The Center for Bio/Molecular Science and Engineering at the Naval Research Laboratory (NRL) evaluated polypropylene nanofiber materials provided by Apollo NanoTech Inc for their potential to remove glycerol and other contaminants from biodiesel preparations. This work was completed in parallel with the development of novel organosilicate sorbent materials directed at these applications (NRL 69-4639; U.S. Provisional Patent Application 62/314,577 March 29, 2017). Solid phase extraction (SPE) offers the potential to reduce the volume of waste water streams currently associated with biodiesel production. The polymer materials evaluated here offer a low cost, scalable material suitable to removal of glycerol from biodiesel.

SOLID PHASE EXTRACTION (SPE) FOR BIODIESEL PROCESSING AND ANALYSIS

INTRODUCTION

Biodiesel is produced by transesterification of animal fat, vegetable oil, or waste cooking oil with an alcohol. Studies focusing on the evaluation of the economic viability of biodiesel [1-4] indicate that production costs are approximately \$0.5 / L, 1.5 times that of petroleum-based diesel, with virgin feedstocks comprising 50 to 70% of costs.[2, 3] While feedstock costs can be reduced through the use of waste cooking oils and similar products, these materials increase the complexity of synthesis and the presence of contaminants.[4] Procurement of water together with liquid and solid waste disposal comprise up to 10% of manufacturing costs,[2, 3] while also influencing the environmental impact of this alternative fuel source. Multiple wash steps for biodiesel purification can generate gallons of waste water for each gallon of usable biofuel. Alternatives to water washes can provide reductions in waste disposal costs and could be used to address the additional contaminants resulting from use of waste-based feedstock sources.

There are several methods than can be applied to development of separation techniques that may replace necessary water wash steps in biodiesel refinement. Unfortunately, the most common methods are poorly suited or face high costs when applied to diesel purification. Distillation is a high energy process and is inappropriate for use with many of the compounds of interest. Liquid/liquid separation produces high volumes of waste water (gallons per gallon of fuel). In addition, it is inappropriate to capture of targets from aqueous media. Crystallization is also a high energy process, and it introduces a number of processing complications. Solid-phase extraction (SPE) is the preferred method of separation for biodiesels. SPE offers flexibility in application format, low volume waste streams, and the potential for reusability. Further, SPE offers the potential to provide advances in both detection and processing of biodiesel. A recent paper demonstrated the potential for SPE in development of a colorimetric method for detection of glycerol content in biodiesel.[5] While another recently argued for the use of SPE in capture of long-chain free fatty acids from aqueous culture media in order to preserve the biocatalyst.[6] In each example, experiments were conducted with resins and sorbents that were developed for other applications. The materials were not designed with a focus on the capture of biodiesel components or function under the conditions of the synthesis/production. As a result, a gap in capabilities and performance exists that can be addressed through careful design/selection of appropriate sorbent materials.

Glycerol, while a contaminant in biodiesel, can be recovered and purified to aid in offsetting the costs of biodiesel production (Figure 1).[3] Glycerol content in fuels can result in fuel tank deposits, injector corrosion, and higher emissions of aldehydes. Free glycerol content provides an indication of the completeness of the reaction, which is valuable information for the producer. This component also provides an indication of the effectiveness of the post-processing procedures and is responsible for storage stability issues as well as leading to deposits in engines. The ASTM standard allows a maximum of 0.02% in the product. At present GC methods are the only standardized technique for determination of this compound. The required instrumentation for this analysis is cost prohibitive for large facilities and unavailable to individual producers. As a result of its importance in determining stability and association with performance issues, glycerol offers a useful starting point in development of suitable SPE methods. Other contaminants in biodiesel products include alcohols, free fatty acids, surfactants, and residual catalyst.

Fig. 1 — Image of (left to right) used cooking oil; as synthesized biodiesel containing glycerol; and purified biodiesel.



Currently, SPE media, also known as dry wash media, use is largely limited to small operations and hobbyists. These media can be used for biodiesel contaminant removal without excessive waste water production. The approach also reduces production time and requires less space when compared to water washing. BD ZorbX and DudaLite (DW-R10®) ion exchange resin are commercial examples of these types of materials. BD ZorbX is a mixture of cellulose fibers from hardwood intended to absorb a variety of contaminants including surfactants, glycerol, and catalyst; Eco2Pure™ is a similar material. DW-R10 is intended as a polishing step following bulk glycerol removal. Claims for this sorbent are removal of surfactants, glycerol, catalyst, and water. Drionex, Purolite® PD206, and Magnesol D-Sol are intended for similar applications.[7]

Nanoporous scaffolds within a macrot textured structure offered an alternative to currently available commercial dry wash media. The materials considered under the NRL effort were hybrid inorganic–organic materials[8-19] in which inorganic and organic moieties are mixed on the molecular scale through the use of bridged polysilsesquioxane precursors.[20] The materials offer large macropores with a templated mesopore structure.[8, 13, 18, 19, 21] While a number of applications have been reported for mesoporous sorbents, additional applications can be facilitated through the use of these hierarchical structures; the macroscale features reduce diffusion limitations and increase access to the mesopore volumes.[22, 23] Materials of this type were previously described for the capture of nitroenergetic and organophosphate targets.[22, 24] Materials developed for application to glycerol capture were synthesized with varying pore wall composition then sulfonated to promote hydrogen bonding interactions with glycerol.[19, 25] Sulfonation of the sorbents provided surface-target interactions similar to those of several commercially available sorbent materials, for example, Amberlite™ B10 DRY. The varied chemical compositions used in organosilicate sorbent synthesis provide differing points within the frameworks for sulfonation as well as varied total site content. The study demonstrated the importance of access to the total surface area for optimal performance characteristics and the trade-offs necessary between total surface area and degree of sulfonation.[19]

For the study described here, polypropylene nanofiber materials provided by Apollo NanoTech Inc are evaluated for their potential utility as solid phase extraction media (Figure 2). Performance in aqueous solution as well as biodiesel preparations is reported.



Fig. 2 — Images of as received nanofiber materials: hydrophilic (A), hydrophobic (B), and sheet type (C) variations. Also shown (D) is an image of the hydrophilic (left) and hydrophobic (right) materials in water.

METHODS

Batch type experiments were used to characterize the binding capacity and affinity of the sorbent materials. Experiments were conducted in 20 mL scintillation vials (EPA Level 3; clear borosilicate glass; PTFE/silicone-lined cap) using a fixed mass of sorbent (indicated in text and figure captions). Target samples (10 mL) were prepared in 18.2 M Ω Milli-Q deionized water or in biodiesel synthesized in-house. Target solutions were added to the sorbents in the vials with a portion of the sample retained for use as a control during chromatographic analysis. Serial dilution of the retained sample was used for generation of a standard curve. Vials were incubated overnight on rotisserie mixers. Samples were filtered using 25 mm Acrodisc 0.2 μ m syringe filters with PTFE membranes prior to processing and analysis. Difference method analysis was applied to determine the target removed from solution.

Analysis of glycerol was based on the method described by ASTM D6584-13.[26] For initial characterization, all samples and control solutions were aqueous; water was removed (5 mL) using a KD Scientific Centrifan PE-T (Model 78-0070). A stock solution of N-methyl-N-(trimethylsilyl)trifluoroacetamide (MSTFA; 160 μ L) was added to the dried samples followed by incubation for 20 min. Heptane (1.6 mL) was then added to the samples, and they were transferred to autosampler vials for GC analysis. GC-MS analysis was performed using a Shimadzu GCMS-QP2010 with AOC-20 autoinjector equipped with a Restex Rtx-5 (30 m x 0.25 mm ID x 0.25 μ m df) cross bond 5% diphenyl 95% dimethyl polysiloxane column. A GC injection temperature of 200°C was used with a 1:1 split ratio at a flow rate of 3.6 mL/min at 69.4 kPa. The oven gradient ramped from 50°C (1 min hold time) to 180°C at 15°C/min and then to 300°C at 20°C/min where it was held for 5 min. For samples prepared in biodiesel, no water removal was necessary. A sample of the solution (100 μ L) was added to MSTFA (100 μ L). All other aspects of the protocol were identical to that described for samples in aqueous solution.

Biodiesel for sorbent analysis was prepared using food grade canola oil purchased at a local supermarket. Food grade canola oil (1 L) was warmed to 50°C on a hotplate. In a separate container, methanol (355 mL) and sodium hydroxide (3.5 g) were mixed. This mixture was slowly added to the warmed oil, and the result was stirred for 2 h (50°C). The reacted solution was moved to a separatory funnel and allowed to settle so that bottom layer of glycerol could be drained. Rotary evaporation was used to remove residual methanol from the final solution and the pH was verified to be neutral. A known concentration of glycerol (spike) was added to this preparation for sorbent evaluation and controls were analyzed using a modification of the protocol described above. For sample preparation, the sorbent containing solution was filtered to remove the sorbent (as necessary). A 100 µL aliquot was added to 100 µL MSTFA. This solution was mixed well and incubated at room temperature for 20 min before addition of heptane (8 mL). The result was transferred to an auto sampler vial for analysis by the GC-MS protocol described above.

Divinylbenzene (DVB) resins were synthesized in a Teflon-lined autoclave reactor (23 mL capacity).[19, 27] For PDVB-2, DVB (1.5 g; Aldrich technical grade, 80%) was added to tetrahydrofuran (15 mL) with water (0.75 mL) and 2,-2'-azobis(2-methylpropionitrile) (0.0375 g; Aldrich, 98%). The reactor was heated at 100°C for 48 h. Following cooling to room temperature, the reactor was opened and the resin was allowed to dry overnight at room temperature followed by complete drying at 100°C. PDVB-3 was synthesized identically with the exception of the water co-porogen used in the PDVB-2 synthesis which was omitted. Ground resin was added to hexane (20 mL) to produce a wet slurry, and sulfuric acid was added (25 mL) for the sulfonation step. The mixture was heated at 75°C for 1 d before addition of water (300 mL). Sulfonated material was collected by vacuum filtration and washed thoroughly with water before drying at 100°C. Sodium exchange was completed by stirring the material in 1 M NaCl (50 mL) at room temperature for 1 d. The resin was then washed with water, collected by vacuum filtration, and dried at 100°C. Sodium exchange for commercial sorbents was completed in the same manner (Na⁺ variants).

RESULTS

Of specific interest are extraction methods for removal of monoglycerides and sterol glucosides, which impact performance and storage of diesels. Quantification of these targets and removal of surfactants and excess catalysts (acids, bases, metal complexes) are also of interest. Finally, recovery of triacylglycerides and long-chain fatty acids has utility in preparation of feed-stocks. Some relevant efforts in this area have been made by other groups. Purolite has adapted an ion exchange resin to the type of dry wash media needed for removal of salts and free glycerin. The formulation has received mixed reviews. The current most favorably rated material is from Eco2Pure. This material will not provide removal of many catalyst contaminants, methanol, or water, and it must be used in conjunction with an ion exchange resin. The primary attractive feature appears to be that the material is cellulose based and is, therefore, considered to be from a renewable source.

The polypropylene materials supplied by Apollo NanoTech Inc were initially evaluated for their capacity to capture glycerol and Triton X-100 from aqueous solution (Figure 3). This is the typical screening employed for initial evaluations of sorbent materials under the work completed by NRL. Under this analysis, the hydrophobic polypropylene materials bound some glycerol while the hydrophilic materials bound glycerol only from experiments using the greatest amount of sorbent material and the highest concentration of target. This result is consistent with expectations for sorbents of this type. The hydrophilic sorbent binds little target due to strong interactions with the water. The hydrophobic sorbent provides sites for partitioning of targets out of aqueous solution. Both glycerol and the surfactant (Triton X-100) are highly soluble in water: Triton X-100 is soluble to 0.1 L/L and glycerol forms a solution in any proportion. Data on Triton X-100 capture is presented in Figure 4.

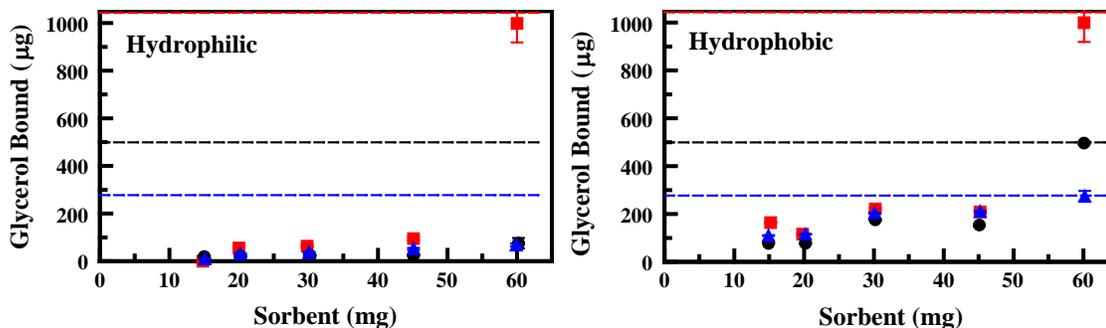


Fig. 3 — Glycerol bound from aqueous solution by two types of polypropylene materials. Varied masses of the sorbents were exposed to a fixed volume of solutions of different initial concentration. Dashed lines indicated the initial target available in the experiment for points of corresponding color.

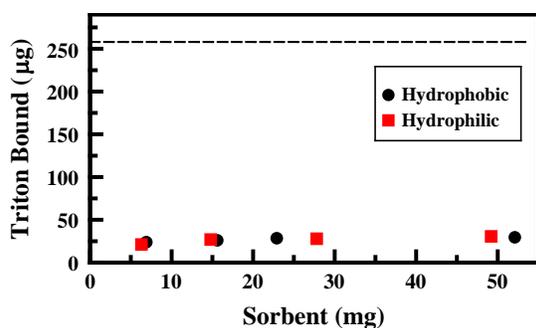


Fig. 4 — Triton X-100 bound from aqueous solution by two types of polypropylene materials. Varied masses of the sorbents were exposed to a fixed volume of solutions of different initial concentration. Dashed lines indicated the initial target available in the experiment for points of corresponding color.

Initial screening was followed by evaluation of the potential for the materials to function as a sorbent in a biodiesel preparation. Biodiesel was synthesized in-house from canola oil and purified following methods typically employed in small batch production; some residual glycerol remained in this baseline material. The biodiesel preparation was spiked with known concentrations of glycerol and adsorption by the sorbents was determined based on differences from the concentrations determined in spiked solutions. This protocol will tend to underestimate the total capacity of the sorbent materials. Distortions will be proportional to the concentration in the original biodiesel preparation; in the absence of a pure standard, this method provides the best estimate of capacity. As shown in Figure 5, the hydrophilic sorbent significantly outperforms the hydrophobic material with both materials binding a significant proportion of the spiked glycerol.

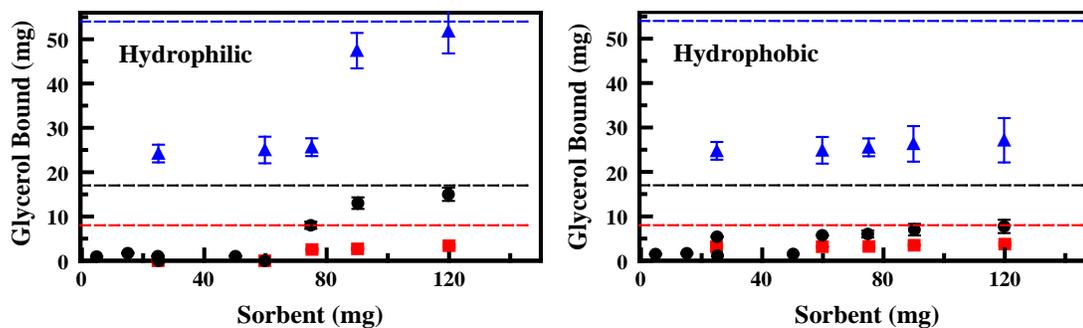


Fig. 5 — Glycerol bound from biodiesel solution by the two types of polypropylene materials. Varied masses of the sorbents were exposed to a fixed volume of solutions of different initial concentration. Dashed lines indicate the initial target available in the experiment for points of the corresponding color.

The behavior observed for the hydrophobic sorbent is expected based on glycerol solubility; glycerol is poorly soluble in biodiesel. In small batch production, a separatory funnel is often used to remove the bulk of the glycerol, based on phase separation between the glycerol and biodiesel components. This process will not remove all of the glycerol from the preparation. This phase separation behavior is the likely mechanism at work in removal of glycerol by the hydrophobic sorbent. The sorbent provides a surface for partitioning behavior. This is similar to the behavior involved in capture and removal of oil from oil/water mixtures that has been described previously (Figure 6). While this behavior will also contribute to removal by the hydrophilic sorbent, the additional capacity noted for this material as well as the nearly 100% removal indicated for higher sorbent concentrations is a result of favorable surface interactions and high surface availability. The calculated glycerol saturation capacity for the hydrophilic sorbent is on the order of 1 g/g.

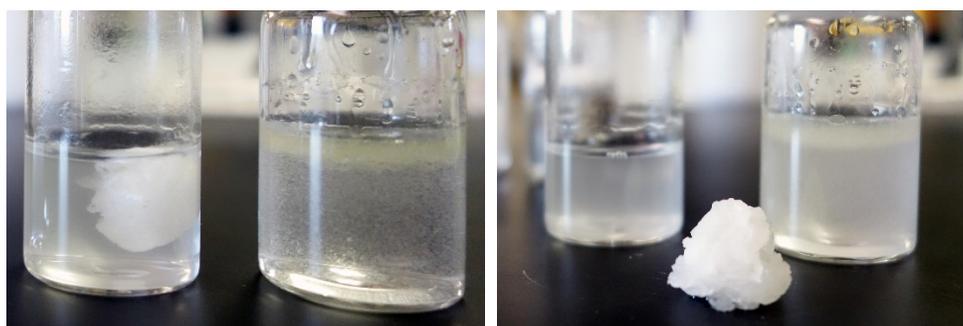


Fig. 6 — Photographs of canola oil and water mixture with and without the hydrophobic sorbent (A). Photograph of hydrophobic material after submersion in oil/water mixture (B).

BD ZorbX and DudaLite (DW-R10®) ion exchange resin are commercial examples of dry wash media. BD ZorbX is a mixture of cellulose fibers from hardwood intended to absorb a variety of contaminants including surfactants, glycerol, and catalyst; Eco2Pure™ is a similar material. DW-R10 is intended as a polishing step following bulk glycerol removal. Claims for this sorbent are removal of surfactants, glycerol, catalyst, and water. Drionex, Purolite® PD206, and Magnesol D-Sol are intended for similar applications. As a point of comparison, commercially available sorbents, BD ZorbX and DW-R10, were evaluated. Attempts to obtain Amberlite™ B10 DRY were unsuccessful. Amberlite gel-type ion-exchange resins are based on a styrene divinylbenzene copolymer backbone. A synthetic process for a mesoporous poly(divinylbenzene) material was adapted from the literature and sulfonated for comparison to the polypropylene nanofiber materials.[27] As shown, the hydrophilic polypropylene material significantly outperforms the other materials considered (Figure 7).

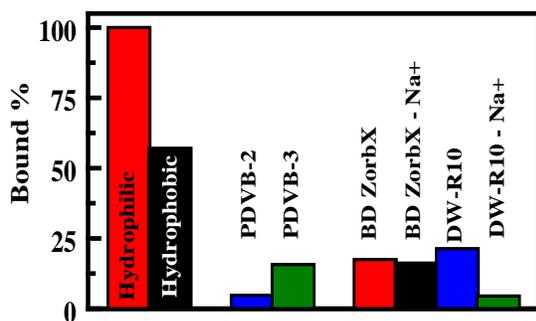


Fig. 7 — Glycerol binding from biodiesel based on identical batch type experiments using 250 μ M glycerol (10 mL) with 30 mg sorbent. The hydrophobic and hydrophilic polypropylene materials are compared to NRL-synthesized poly(divinylbenzene) materials as well as commercial materials variants.

CONCLUSIONS

Solid phase extraction (SPE) offers the potential for effective and efficient recovery methods for synthetic components previously considered expendable. It offers the opportunity to reduce the volumes of waste water streams and, therefore, the cost of waste disposal. SPE also offers large energy savings over many traditional purification approaches, and it is highly amenable to small scale production processes. Currently, dry wash media use is largely limited to small operations and hobbyists. The Apollo NanoTech Inc hydrophilic polypropylene nanofiber material offers significant potential in advancing the state of solid phase extraction materials suitable to use in biodiesel preparation. Beyond the results reported here, sulfonation of the materials may produce additional glycerol binding capacity as well as affinity for other targets.

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