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Research article

From orchids to biodiesel: Coco coir as an effective drywash material for biodiesel fuel

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A B S T R A C T

Raw biodiesel requires purification to remove excess methanol, unreacted and/or partially reacted starting material(s), and residual catalyst. The common practice for biodiesel purification is a series of water washes. These water washes are time consuming, generate a large aqueous waste stream, and can lead to saponification and subsequent emulsion formation. To eliminate water washes, solid materials which are capable of purifying the biodiesel after a short residence time are currently the subject of active investigation. Herein, we investigate the use of coco coir, a product of coconut husks commonly used as orchid planting material, as a bio-derived, biodegradable, and inexpensive drywash material for biodiesel fuel. Overall, we find that coco fiber (1) removes soap concentrations of > 3000 ppm in one pass through the column; (2) treats raw biodiesel at volumes which meet or exceed current industry standards; (3) is stable and effective for a time period greater than five years; (4) does not raise free fatty acid levels above acceptable levels; (5) does not add Ca^{2+} or Mg^{2+} to the purified fuel; (6) reduces methanol to acceptable levels; and (7) removes free glycerol, even when biodiesel samples are spiked with artificially large quantities of free glycerol.

1. Introduction

As petroleum reserves diminish, there is an increasing focus on preparing renewable fuels. One of these renewable fuels is biodiesel, the generic name for fatty acid methyl esters (FAMEs). Biodiesel is prepared in a straightforward, simple procedure from a variety of triglyceride feedstocks. On account of its renewable nature, reasonable cost, and simple preparation, biodiesel production is increasing rapidly on the global scale. In the United States alone, biodiesel production totaled 2.2 billion gallons in 2016 [1].

The most common method for preparing biodiesel is a base-catalyzed (usually NaOH or KOH) transesterification of triglycerides with methanol. After complete reaction, this method yields three FAME molecules and one glycerol molecule per triglyceride molecule that reacts. The biodiesel reaction mixture that is produced via this base-catalyzed method commonly contains a mixture of excess methanol, residual catalyst, unreacted and/or partially reacted starting material, and soaps that can be generated during the reaction. The soaps that are generated consist of the alkoxide form of the fatty acid paired with the cation from the strong base catalyst. These soaps are commonly formed when water is present during the biodiesel synthesis reaction.

Immediately after preparation, the biodiesel reaction mixture is referred to as "raw" biodiesel. The raw biodiesel must be purified in order to meet the ASTM standards required for biodiesel fuel to be marketable (ASTM D6751 - 15ce1 Standard, 2015). The most common purification method for raw biodiesel is a repetitive water wash (sometimes carried out with a low concentration of aqueous acid) [3]. This is a time-consuming process, taking several hours to several days, which results in an aqueous waste stream of 0.2–3.0 times the volume of raw biodiesel being washed [4]. This aqueous waste stream is known to have high chemical and biological oxygen demands and contain oil, soap, methanol, and glycerol [5]. As yet another drawback, the water added to wash the raw biodiesel can form an undesired soap byproduct with remaining NaOH in the biodiesel reaction mixture. This decreases the yield of biodiesel and increases the complexity and timescale of the purification process. In addition, in regions where water is in short supply, using large volumes of water to purify a fuel is undesirable.

In light of these concerns, a method for biodiesel purification that does not involve a water wash is appealing. These methods are often referred to as drywash methods, and their uses were recently reviewed [6–9]. The primary drywashing strategies currently reported in the literature are rely on adsorption, ion-exchange processes, and

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membrane filtration.

The adsorption materials explored up to this point have generally been inorganic compounds or biosorbents [3,6,10,11]. The adsorption process simply retains the target molecules on the surface of the material. These materials can be loaded into a stationary column and have biodiesel is passed over them, or they can be agitated in a solution of raw biodiesel and then separated out. Adsorbent materials are replaced with new material once the original material is saturated with the target molecules adsorbed from raw biodiesel.

The simplest and least expensive adsorbent materials are bio-adsorbents based on wood chips (sawdust) mixed with proprietary resin beads [12,13]. Several inorganic adsorbent materials have also been studied as drywash materials, including silica [14–17]) and magnesol [8,14]. Another class of materials which have been used as a biodiesel drywash materials are ion-exchange resins [8,14,18,19]. While each of these drywash materials have been shown to remove impurities such as soap and glycerides from raw biodiesel, they all suffer from major drawbacks such as extra filtration steps, requiring time and energy intensive heating steps, generating additional waste, and using non-biodegradable materials. These factors add expense and risk to the biodiesel manufacturer and are incongruous with several of the tenants of green chemistry [20]. Table 1 shows the cost, claimed treatable volumes, and disposal characteristics of the adsorbent and ion-exchange materials discussed thus far, as well as a comparison to the coco coir studied herein.

Another method for biodiesel drywashing is membrane filtration. Membrane filtration is widely used in water purification and gas separation, and has been attracting increasing attention for the purification of raw biodiesel. These membranes can be ceramic [21,22] or gel/polymer in nature [23,24]. The purification efficacy of a gel or polymer membrane can be affected by temperature, pressure, composition, and flow velocity of the material through the membrane. Additionally, the choice of an organic polymer gel membrane versus a rigid inorganic membrane can strongly influence both the extent and the ease of purification. In many cases, smaller pore size increases biodiesel purity but decreases throughput of biodiesel through the membrane. This can slow production in large-scale facilities, which is undesirable.

All of the materials and processes studied to date are not sustainable long-term solutions to the biodiesel purification problem on account of cost, adsorbent lifetime, and the additional time, energy, and chemical inputs required to activate many of the materials. An ideal drywash material for biodiesel would be readily available, bio-derived, biodegradable, renewable, inexpensive, and effective at removing soaps, methanol, and free glycerol. As a starting point, and with the aim of developing a adsorbent material easily accessible to the at-home biodiesel producer, we considered natural fibers which were available at local garden centers. Of these natural fibers, the best candidate was coco coir. Coco coir has been shown to be an effective adsorbent material for water purification [25] and coco coir dust has been used as an adsorbent of methylene blue cationic dyes from aqueous solution [26]; additionally, the used coco coir adsorbent material may possess post-sorption value [27].

Table 1
Comparison of soap removal and cost for 1 kg samples of commercially available biodiesel drywash materials compared to the coco coir studied herein.

Material	Treatable volume	Approximate cost for 1 kg	Biodegradable?
Eco_2Pure	300–600 L	$11	Partially
BD Zorb	210–750 L	$6	Yes
Amberlite BD10 Dry	1000–1800 L	$19	No
Purolite PD 206	486 L	$22	No
Thermax T45 BD	607 L	$27	No
Coco coir	> 375 L	$3	Yes

Coco coir is a heterogeneous natural fiber collected from coconut husks. Coco coir is inexpensive and durable, and consequently is used for everything from upholstery padding to brushes to a planting medium for orchid cultivation [28]. In its commercially available form, coco coir consists of three distinct materials: coco pith, coco fiber, and coco chips. The pith is sponge-like material that is thought to participate in ion-exchange reactions. The fiber is a hair-like, largely cellulosic material, while the coco chips are similar in size and function to clay pebbles [29]. This heterogeneous coco coir is readily available at most garden supply stores at a fraction of the cost of commercial biodiesel drywash materials (see Table 1). The coco coir examined herein is entirely derived from coconut husks and as such is biodegradable.

Herein, we present our evaluation of coco coir as a readily available, inexpensive, biodegradable, renewable, and effective drywash material for biodiesel. To this end, we examined coco coir's ability to remove soap, methanol, and free glycerol from raw biodiesel. As part of this study, we considered both the treatable volume of biodiesel and long-term stability and efficacy of the material. In addition to removing the undesirable soap, methanol, and glycerol, it was also important to ensure that additional components did not leach from the column material itself. Consequently, we tested the drywashed biodiesel for free fatty acids and alkali earth metal ions known to be present in coco coir (Ca^{2+} and Mg^{2+}). Overall, we find that coco coir serves as an effective, low-cost, renewable, hardy drywash material for purifying raw biodiesel.

2. Materials and methods

2.1. Materials

Raw biodiesel was supplied by Springboard Biodiesel, LLC, Chico CA. The feedstock for Springboard's biodiesel is commingled used cooking oil from local eateries. Springboard's production method uses a sulfuric acid pre-treatment to esterify any free fatty acids present and a base catalysis step for the primary transesterification reaction. Samples were collected at this point, before any of Springboard's standard purification methods. Raw biodiesel was also supplied by Sierra Nevada Brewery, Chico CA. The feedstock for Sierra Nevada's Brewery's biodiesel is waste cooking oil from their on-site restaurant. This biodiesel is manufactured using a Springboard Bio-Pro processor, and thus undergoes the some production process as the biodiesel produced in Springboard Biodiesel's facility.

Nanopure water was produced by an in-house filtration system. Hydrochloric acid, sodium hydroxide, methanol and isopropanol were purchased from Sigma Aldrich in 99% or greater purity and used without further purification. Phenolphthalein indicator was prepared as a 1 mass % solution in ethanol. Bromophenol blue indicator was prepared as a 0.4 mass % solution in distilled water. The hydrochloric acid used to titrate for soap content was standardized with sodium carbonate and the sodium hydroxide used to titrate for free fatty acid content was standardized by titrating potassium hydrogen phthalate. Both of these standardizations used a phenolphthalein endpoint.

A commercially available biodiesel drywashing product, Eco_2Pure, was donated by Springboard Biodiesel. The coco coir studied herein was purchased at a local garden supply center. Manufactured by CocoTek, the coco coir was purchased as a brick of compressed coco coir.

2.2. Coco coir evaluation and column preparation

2.2.1. Coco coir surface area measurement

The Brunauer-Emmett-Teller (BET) surface area of the coconut husk sample was measured on a commercial gas adsorption analyzer (Micromeritics Gemini V) using nitrogen as the adsorbate at liquid nitrogen temperatures (77 K). The BET surface area was determined from the gas adsorbed between relative pressures (P/P_0) of 0.05 and 0.28 (a larger isotherm was collected between P/P_0 of 0.015 and 0.98).