



A gasoline-grade biofuel formed from renewable polyhydroxybutyrate on solid phosphoric acid



Shimin Kang, Jian Yu*

Hawaii Natural Energy Institute, University of Hawaii at Manoa, Honolulu, HI 96822, USA

HIGHLIGHTS

- Bacterial biopolyester is used as a type of new feedstock for renewable fuels.
- A gasoline-grade liquid oil is formed on solid acid catalyst under mild conditions.
- The oil is a good source of bio-based alkenes and aromatics.

ARTICLE INFO

Article history:

Received 4 May 2015

Received in revised form 30 July 2015

Accepted 31 July 2015

Available online 5 August 2015

Keywords:

Polyhydroxybutyrate

Solid phosphoric acid

Biofuels

Bio-based aromatics

Renewable gasoline

ABSTRACT

Polyhydroxybutyrate (PHB) is an energy storage material formed from renewable feedstock in many bacterial species. The biopolyester ($C_4H_6O_2$)_n was degraded, deoxygenated and reformed into hydrocarbon oil (C_6 – C_{18}) on solid phosphoric acid (SPA) in one-pot reaction. The reaction started at 213 °C and completed below 240 °C as measured with a differential scanning calorimeter. In addition to the oil, other products included carbon dioxide (CO₂), propylene (C₃H₆), water (H₂O) and some char-like solid. The mass yields in a typical reaction were determined with a total mass recovery of 94 wt%. About 80% of oxygen in PHB was removed as CO₂ via decarboxylation. By using a gas chromatograph–mass spectrometer, the oil composition was analyzed according to the chemical structure and carbon number of major compounds. In contrast to conventional biofuels derived from plant biomass, the PHB–oil has a high content of alkenes or aromatics, depending on the solid acid catalyst. The catalyst properties that affected the reaction include the calcination temperature in catalyst preparation, the catalyst dosage in the reaction, the total acid and free acid contents of fresh or used catalyst, and working time when the catalyst was repeatedly reused. The hydrocarbon oil (30 wt% yield) was separated into two fractions according to their boiling temperature range: a light oil (bp 40–240 °C) with 23 wt% yield and a heavy oil (bp 240–310 °C) with 7 wt% yield. The light oil has the same elemental composition and high heating value (HHV 41.4/kJ) of a commercial gasoline and the heavy oil (HHV 38.4 MJ/kg) has the similar elemental composition of biodiesel. The oil is a good source of bio-based alkenes and aromatics that can improve the performance of bio-based fuels in modern motor engines.

© 2015 Elsevier Ltd. All rights reserved.

1. Introduction

With growing concerns over energy security and climate change, renewable feedstocks such as starch, oil and lignocellulose are being increasingly used to produce transportation fuels including gasoline and diesel [1–3]. Ethanol, for example, is a biofuel produced from sugar and starch through microbial fermentation. Because of its high oxygen content (34.8 wt%) and relatively low energy content (HHV 29.7 MJ/kg), ethanol is primarily used as an additive in gasoline [4,5]. To satisfy modern high performance

automotive engines, today's gasoline must meet specific national and local standards. Unleaded gasoline, for example, contains a substantial amount of aromatics that replace lead-containing additives and maintain a high octane number and energy content [6–8]. Because of the high oxygen content in biomass (up to 50 wt%), deoxygenation and reforming of renewable feedstock into hydrocarbons of desired chemical composition is a great technical challenge. There are several routes to convert biomass into a “drop-in” hydrocarbon fuel, usually involving multiple catalytic reactions under severe conditions [1–3,9,10]. For example, catalytic fast pyrolysis at high temperatures (400–650 °C) is the first step to liquefy the biomass, and the liquid is further upgraded through multiple reactions including hydrotreatment and catalytic

* Corresponding author.

E-mail address: jianyuan@hawaii.edu (J. Yu).

cracking. Different catalysts in multiple reactors under specific reaction conditions including high pressure hydrogen are needed in the reforming process, resulting in high costs of equipment and operation [2,11–13]. Serious coking at high temperatures often results in quick deactivation of the catalysts [14–16]. Alternative feedstock and new processing technology could provide solutions to the challenge.

Like starch and oil accumulated in plants, polyhydroxybutyrate (PHB) is an energy storage material accumulated in many bacterial species. The biopolyester is synthesized by bacterial cells from renewable feedstock (glucose, glycerol, organic acids, etc.) or CO₂ and H₂ [17–19]. Under controlled conditions, the microbes can accumulate up to 80% of PHB in dry cell mass [19]. Recently, we reported that PHB could be conveniently reformed into hydrocarbon oil in aqueous phosphoric acid solutions (50–100% H₃PO₄) at mild temperatures (200–240 °C) [20]. It was also found out that water was a byproduct of PHB deoxygenation and hence water might affect the yield and composition of hydrocarbon oil [21]. With a concentrated polyphosphoric acid, however, little oil was formed except char-like solid. Solid phosphoric acid (SPA) is a catalyst commonly used in oligomerization and alkylation of alkenes in hydrocarbon reforming [22–24]. The solid acid does not contain water but contains active phosphoric acid species (i.e. H₃PO₄, H₄P₂O₇ and H₅P₃O₁₀) fixed in silicon matrix [23–26]. The acid content of SPA can therefore be tailored to investigate PHB reforming. In this work, SPA was first time used to reform PHB in one-pot reaction. Since the melting temperature of PHB is around 180 °C [27,28], the reforming reaction most likely involves two phases at the reaction temperature; a liquid phase of PHB/oil and a solid phase of SPA catalyst. For confirmation, differential scanning calorimetry was first time used to measure the reaction temperature accurately. In addition, PHB recovery and purification from microbial cell mass is a high cost operation and may determine the price of PHB feedstock [29]. This work also investigated if a crude PHB (~80 wt%) with high bacterial residue could be directly reformed on SPA without purification.

2. Material and methods

2.1. Materials

Celite kieselguhr (Celite®577 fine, filter aid, calcined) and polyphosphoric acid (115% H₃PO₄ basis) were purchased from Sigma–Aldrich (St Louis, MO, USA). Two types of polyhydroxybutyrate (98 wt% PHB and 87 wt% PHB) were kindly provided by Bio-On (Bologna, Italy) and used as PHB and crude PHB thereafter. Biomass of *C. necator*, a typical PHB-producing bacterium, was prepared by extracting PHB in hot chloroform till the PHB content of residual biomass below 2 wt% [30].

2.2. Preparation of solid phosphoric acid catalysts

The solid phosphoric acid (SPA) catalysts were prepared by following a published protocol [23,24]. Celite kieselguhr and polyphosphoric acid were thoroughly mixed at a mass ratio of 2.7:1 and then heated at 220 °C for 20 min. The solid acid mixture was calcined in air at preset temperatures for 25 min. The SPA catalysts calcined at 420 °C, 560 °C and 720 °C were labeled as SPA420, SPA560, and SPA720, respectively. Finally, the solid acids were ground into fine powders for good mixing with PHB powders.

2.3. Characterization of solid phosphoric acid

The acid content of SPA was determined by titration with 0.2 M sodium hydroxide solution [23,24]. The solid acid was first soaked

in water for 10 min under ambient conditions and then recovered on a filter paper. The amount of acid released into water was determined by titration to pH 4.62 and referred as free acid. The total acid was determined by boiling the SPA powder in water for 60 min to hydrolyze the silicon ortho- and pyro-phosphates, thereby releasing the fixed phosphoric acid from silica. The solution was quickly cooled down to room temperature and titrated to pH 4.62. The surface topography of fresh and used SPA catalysts were analyzed with scanning electron microscopy (SEM, Hitachi S-4800) and energy dispersive X-ray spectroscopy (EDS, Oxford INCA X-Act).

2.4. Differential scanning calorimetry (DSC) analysis

The solids of PHB, SPA420, and their mixture were heated in a differential scanning thermal analyzer (TA Instruments, USA) under a N₂ stream of 50 mL/min. The temperature program was started at 25 °C, increased to 100 °C at 5 °C min⁻¹, and further increased to 240 °C min⁻¹ at 2 °C min⁻¹ and maintained at 240 °C for 2 min.

2.5. Oil formation from PHB on solid phosphoric acid

2.5.1. Reaction for oil collection and separation

A pre-determined amount (70 g in total) of SPA catalyst and PHB powder were mixed in a 180 mL pyro-beaker and put in a 600 mL unstirred thermal reactor (Parr Instrument Co., Ltd., USA). A typical reaction was referred in this paper when the mass ratio of SPA420 to PHB powder was 1:1. After N₂ flush, the reactor was heated from room temperature to 240 °C in about 45 min and maintained at 240 °C for 6 h. After the reaction, the reactor was cooled down in air to 40 °C in about 20 min. The temperature and pressure were recorded when gas samples were taken for composition analysis. The reactor was then connected to a cooling and condensing system as shown in Fig. 1. Under a N₂ stream, the reactor was heated slowly and the products were evaporated and condensed in the collector. The N₂ flow rate was controlled so that single bubbles came out from the cooling system. The distillation was divided into two stages. In the first stage, the reactor was heated from 40 °C to 240 °C in about 2 h and the collected liquid was labeled as light-oil (bp 40–240 °C). In the second stage, the temperature was increased from 240 °C to 310 °C and maintained at 310 °C for about 2 h. The collected liquid was labeled as heavy-oil (bp 240–310 °C). Aqueous solutions formed in the reaction were also collected and separated from the oils in a separating funnel.

After the liquid products were recovered with the distillation, the reactor was cooled down to room temperature again. The SPA catalyst in the pyro-beaker was collected in the form of dry solid. Some char-like byproducts were deposited on SPA and its content was determined based on weight increase of SPA solid after the reaction. A small amount of char-like byproducts was also collected outside of the pyro-beaker, but negligible to the total mass recovered. The used SPA catalyst was heated in air at 420 °C for 25 min to test if the char-like deposit could be removed.

2.5.2. Reaction for oil composition analysis

To determine the composition of whole liquid oil (light-oil plus heavy-oil), the reaction was also conducted in a small (20 mL) polytetrafluoroethylene (PTFE) reactor. Pre-determined amount of PHB powder and SPA catalysts (2 g in total) at different mass ratios were put in PTFE containers and sealed in stainless steel cylinders. The reactors were left in a thermostat oven at 240 °C for 6 h. After reaction, the reactors were quickly cooled down under tap water. The products were dissolved in methylene chloride for composition analysis. The SPA catalyst was washed by

Download English Version:

<https://daneshyari.com/en/article/205549>

Download Persian Version:

<https://daneshyari.com/article/205549>

[Daneshyari.com](https://daneshyari.com)