Ethyl 3-Ethoxybutyrate, a New Component of the Transportation Renewable Fuel Portfolio

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21 ABSTRACT

22 The vast majority of energy that powers our global economy is from combustion of fossil fuels
23 with the unintended consequence of increased deposition of carbon dioxide in the atmosphere
24 and oceans. The scientific and technical challenges for the energy sector are to develop
25 renewable energy sources that are sufficient to meet human energy consumption, are
26 economically viable, and are ecologically sustainable. We investigated ethyl 3-ethoxybutyrate
27 (EEB) as a fuel oxygenate in ultra low sulfur diesel (ULSD) with a bench-scale research engine
28 and determined its economic potential as a renewable fuel with technoeconomic modeling using
29 wastewater treatment plant biosolids as the feedstock for poly-3-hydroxyalkanoates (PHB), a
30 bacterial storage polymer from which EEB can be synthesized. EEB blended well with ULSD,
31 and cetane values of 10% and 20% v/v EEB-ULSD blends exceeded 40. A diesel internal
32 combustion engine fueled with 5%, 10%, and 20% EEB-ULSD blends met or exceeded all tested
33 transportation diesel fuel emissions criteria. Inedible organic feedstocks may be used to produce
34 PHB; and thus, EEB might contribute to carbon reductions without compromising performance
35 or air pollutant emissions. However, further research is needed to determine its role in the
36 overall fuel portfolio.

37

38 *Keywords* Biofuels, Criteria pollutants, Fuel oxygenates, Technoeconomic modeling

1. Introduction

Economically viable and ecologically sustainable renewable energy sources that meet human energy consumption rates are needed [1,2]. Globally, liquid fuel production in 2008 was 86 million barrels per day and is predicted to reach 112 million barrels per day by 2035 [3]. Biofuel production is predicted to triple over this period, yet its contribution to the liquid fuel inventory is projected to be minor if limited to existing methods of biofuel production (1.8% in 2008 and 4.2% by 2035) [3]. Biofuel production technologies that rely on well understood biological and chemical principles and support strategies that can be rapidly deployed have the potential to impact biofuel markets in the near-term when the environmental benefits are most critically needed [2].

Biodiesel is currently the only commercially available diesel oxygenate made from renewable carbon sources. While there are many advantages to biodiesel, it also has several drawbacks including plant and animal based biodiesel production is limited by environmental sustainability issues, algae based biodiesel production is limited by production cost, high cloud point temperatures and increased nitrogen oxides (NO_x) emissions result in technical limitations of biodiesel [4]. Other potential diesel oxygenates under investigation include alcohols, ethers, acetone, and emulsions with water [5-7]. However, practical concerns such as corrosion and low flash point will likely limit the commercial viability of low molecular weight oxygenates [8].

The purposes of the effort reported here were to introduce ethyl 3-ethoxybutyrate (EEB) as a novel, renewable diesel oxygenate and to show a potential pathway of EEB production. This and another article are the first reports of using EEB as a fuel [9]. Prior studies of EEB were limited to its synthesis and stereochemistry [10-13]; however, methyl 3-hydroxybutyrate, which originates from the same precursor (poly-3-hydroxybutyrate (PHB)) as EEB, was investigated as

a biofuel additive [14,15]. EEB can be produced from PHB under acidic conditions after esterification with ethanol via ethoxylation of ethyl 3-hydroxybutyrate [16] or synthesized under caustic conditions via addition of ethanol to ethyl crotonate (produced during esterification of PHB via dehydration of 3-hydroxybutyrate) [10].

PHB and the related poly-3-hydroxyalkanoate (PHA) are produced from short chain fatty acids (SCFA) which enables many inedible organic wastes to be used as feedstocks [17-21]. PHB and PHA are produced naturally by many taxa of bacteria grown under carbon replete conditions, when cellular replication is limited by a nutrient or a redox imbalance [22]. A variety of waste organic feedstocks can be used in their production, and industrial-scale operations are currently in place where EEB can be produced. For instance, industries that are favorable for development of PHB and PHA accumulation unit operations include wastewater treatment plants, food processors, and paper mills [22].

2. Materials and Methods

2.1. Fuel characteristics of EEB.

Synthesis and purification of EEB used during this study were described elsewhere [9]. Cetane (CN) and flash point were determined with ASTM certified analyses by a contract testing company (Midwest Laboratories, Inc., Omaha, NE).

2.2. Engine tests with EEB.

The research engine, its setup, and calculations used to determine heat release were previously described [23-25]. Briefly, EEB blended with ultra low sulfur diesel (ULSD) at different volumetric ratios (5%, 10%, 20%, 30%, and 50% EEB v/v) was tested in a 517cc Hatz

single-cylinder research diesel internal combustion engine. Speed was held constant while fuel delivered to the engine was varied in a low-high-low sweep to produce IMEP values that spanned the engine's operating range. Once the engine reached steady state at each load point, data were recorded and averaged over 250 cycles. Data were acquired as low-speed (time-based) data and high-speed (crank-angle based) data using Indicom software in conjunction with multiple F-FEM-AIN fast front end modules, a microIFEM piezo amplifier, and an Indimodul signal acquisition and processing unit (AVL LIST GmbH). Blend specific calorific data for engine analysis was based on the chemical composition of EEB, and the calorific value for 100% EEB was estimated to be equal to soy biodiesel (37.5 MJ/Kg). Emissions were collected using a CLD NO_x analyzer (California Analytical Instruments), flame ionization hydrocarbon analyzer, non-dispersive infrared three-gas analyzer, and opacity smoke meter (AVL LIST GmbH).

Data were normalized to fuel flow rate and indexed to 100% ULSD tests run proximal to the blend test to compare the different EEB-ULSD blends. Statistical analysis to compare EEB blended fuels with 100% ULSD was with the `pairw.anova` function of `asbio` package (0.4-11) in R (3.0.1) using the Tukey method and 95% confidence intervals. Low and high loads were functionally defined as the first and third tertiles for each blend (low load conditions, speed = 1800 rpm, fuel flow rate = 0.09 – 0.19 g/s, and high load conditions, speed = 1800 rpm, fuel flow rate = 0.23 – 0.31 g/s). Data in tertiles of low and high loads were engine test specific (low load data for all blends ($n = 4$); high load data for 5% EEB ($n = 5$), 10% EEB ($n = 3$), 20% EEB ($n = 3$), and 30% EEB ($n = 4$)). ULSD low load ($n = 4$) and high load ($n = 3$) data were collected on the same day as data collected for 5%, 10%, 20% EEB-ULSD blends. Data collected for the 30% EEB-ULSD blend were collected 5 d prior to ULSD low load ($n = 3$) and high load ($n = 4$) data.

2.3. Technoeconomic model of EEB production.

Technoeconomic modeling was performed to understand the cost efficiency of producing EEB from wastewater sludge and key cost drivers. The modeling was done with Superpro Designer leveraging default, built-in models for wastewater treatment plants (WWTP) and biofuel production. A WWTP system that processed $4800 \text{ m}^3 \text{ d}^{-1}$ wastewater and produced 4800 kg d^{-1} biosolids was modeled to determine EEB production potential at a WWTP-based biorefinery. The technoeconomic model included SCFA production from fermentation of biosolids, PHA production, and EEB production. For biosolids fermentation, our modeled SCFA production was based on previously reported findings that showed high production of SCFAs from WWTP secondary sludge at high pH [21] (SCFA production was expressed as acetate equivalents). For PHA production, an anaerobic-aerobic process was modeled on previous studies [26,27] (PHA production expressed as PHB equivalents). A hydraulic retention time of 6 hr and a sludge retention time of 8 days were assumed. In the modeled system, longer sludge retention time compared to hydraulic retention time was realized via clarification and sludge recirculation. Modeled EEB production conditions included dehydrating the PHB as water inhibits the reaction and were based on conversion of PHB to ethylated monomers for 2 hr at 140°C with ethanol and sulfuric acid (15% w/w) [16].

3. Results

3.1. EEB diesel fuel properties

CN for blends of 10%, 20%, and 40% v/v EEB with ULSD were 43.3, 41.8, and 38.5, respectively. Thus, the 10% and 20% EEB-ULSD blends met the CN specification for on-road

diesel fuel (specified minimum CN is 40). The flash point of EEB (56 °C) was within 4 °C and 5 °C of the lower limit of the flash point for biodiesel and diesel suggesting that EEB blended fuels may require a shift to higher temperature distillate fractions to compensate for the lower flash point of EEB.

3.2. Internal combustion engine performance and emissions

EEB-ULSD blends up to 50% EEB v/v were evaluated for engine performance and emissions with a Hatz 517cc single-cylinder diesel research engine. Engine performance characteristics showed some variation between November 2010 and April 2011 for the test runs with ULSD (Fig. 1). EEB-ULSD blends of 5%, 10%, 20%, and 30% exhibited stable combustion that was comparable to ULSD combustion as indicated by several combustion parameters including exhaust and peak cylinder temperatures, indicated mean effective pressure, the coefficient of variance of indicated mean effective pressure, and crank angles at the start of combustion, 50 % fuel combustion, and the angle delta between 10 % and 90 % combustion (Fig. 1). Even though the lower CN of EEB retarded the start of combustion of the EEB-ULSD blends (Fig. 1(d)), the start of combustion of ULSD and the 5% and 10% blends were statistically comparable (within +/- 15% confidence interval) when modeled using a 2nd order polynomial. The 50% blend failed to combust under low load conditions (speed = 1800 rpm, fuel flow rate = 0.135 – 0.145 g/s), indicating the existence of a combustion-limited maximum blend volume (Fig. 1).

Indexing the EEB-ULSD blends to 100% ULSD revealed that EEB at higher blends influenced engine performance (Fig. 2). The 20% EEB-ULSD blend produced significantly different engine performance as measured by SOC and CA10-90 under low-load conditions, and

CA10-90 was significantly lower under high-load conditions for the 20% EEB-ULSD blend (Table 1). The impact of higher blends on engine performance was more pronounced with the 30% EEB-ULSD blend where IMEP, CA10-90, and IP were statistically different under low-load and high-load conditions and SOC was statically higher under high load conditions.

Indicated specific fuel consumption (ISFC), volumetric efficiency, and thermal efficiency were estimated for ULSD and EEB-ULSD blends (Fig. 3). Fuel consumption and efficiencies for ULSD and EEB-ULSD blends of 5%, 10%, 20%, and 30% were comparable despite variation between November 2010 and April 2011 test runs. Indeed, EEB-ULSD blends had ISFC values that were statistically comparable to ULSD, although EEB-ULSD blends generally showed a reduction in ISFC values at low loads (Fig. 4).

Criteria pollutants (i.e., PM, CO, and NO_x) and exhaust gases (i.e., O₂, HC, and CO₂) were measured for ULSD and EEB-ULSD blends (Fig. 5). Criteria pollutants showed some variation between November 2010 and April 2011 for the test runs with ULSD, however little variation was observed for the exhaust gases except an increase for the April 2011 low fuel flow HC measurements. PM generally decreased whereas CO and HC generally increased with increasing amounts of EEB in the fuel (Fig. 3). Oxygen, CO₂ and NO_x showed little response to EEB blend level except for the 50% blend which produced a consistently distinct emissions profile for all measurements.

The effect of lower cetane number on emissions was largely offset by the effect of fuel oxygen (Fig. 4). For instance, under low-load conditions, all of the EEB-ULSD blends produced equivalent or less PM compared to ULSD, and the 30% blend produced significantly less PM, NO_x, and carbon dioxide (CO₂) compared to ULSD (Table 1). Similar results occurred under high-load conditions; and again, the 30% blend produced significantly less PM, NO_x, and CO₂

compared to ULSD. Otherwise, emissions data for EEB-diesel blends were statistically equivalent to ULSD, except the 20% blend produced significantly less CO₂ under high-load conditions. Combined, the combustion and emissions data indicate that addition of 5% or 10% EEB to ULSD as an oxygenate introduces renewable carbon without negatively affecting fuel consumption while improving the fuel's exhaust emissions profile.

3.3. Technoeconomic modeling of potential EEB production

Our findings indicate that EEB is a possible renewable fuel if large quantities of EEB can be sustainably and cost-effectively produced. One possible strategy is the production of EEB from PHA-rich biomass at WWTP [28]. We modeled an EEB production process that used WWTP biosolids as the feedstock for PHA synthesis. For modeling, we assumed that acetate was produced from biosolids fermentation and that the homopolymer, PHB, was accumulated in a separate unit operation. The model output under these conditions was 1,117 kg acetate/hr, 75 kg volatile suspended solids/hr, and 323,745 kg water/hr for biosolids fermentation, which in turn resulted in predicted polymer production outputs of 360 kg PHB/hr, 1,813 kg volatile suspended solids/hr, and 8,694 kg water/hr. The estimated cost to produce and extract a mixture containing ethyl crotonate (EC), ethyl 3-hydroxybutyrate, and EEB from PHB reacted with ethanol under acidic conditions at a WWTP in the United States was \$1.24/L. This estimate was in general agreement with the production of methyl 3-hydroxyalkanoate gasoline oxygenates [14,29]. Our cost estimate was based on production in the United States with domestically supplied equipment. Global supply chain efficiencies would likely reduce the overall costs of EEB since tanker transportation of fuel adds little to its cost [30]. Moreover, WWTPs are near both large metropolitan areas and rural communities, and thus WWTP-based biorefinery capacity can

expand to process other feedstocks that are local to the service area.

4. Discussion

The impact of biodiesel on diesel engine performance and emissions has been intensely studied [31-35]. EEB properties as a diesel oxygenate were distinctly different from biodiesel, although some attributes were comparable depending on load. For instance, ISFC was lower for EEB-ULSD blends under low-load conditions and slightly higher under high-load conditions. Biodiesel is typically reported to increase fuel consumption compared to diesel [31]. EEB was generally comparable with biodiesel as a diesel oxygenate for PM across load condition. EEB and biodiesel were also comparable for CO under high-load conditions, yet they produce opposite results for THC under high-load conditions. Reductions in NO_x occurred with higher blend levels and EEB co-blended with biodiesel might serve to mitigate elevated NO_x production associated with unsaturated biodiesel. Indeed, the ethoxy moiety may be the source of NO_x reduction as observed with ether-diesel blends [36-38]. Moreover, the ethoxy moiety influences the melting point of EEB such that cloud point should not be a concern for EEB blended fuels, and EEB might be added to high cloud point fuels. However, these initial studies were with a research engine in a laboratory setting, and fleet-based studies are needed to assess EEB-ULSD blend performance under light-duty and heavy-duty engine cycles. Furthermore, detailed engine cycle analysis, including full rate of heat release profiles, may be done to provide greater insights into performance of potentially commercial blends of EEB-ULSD with different engine configurations.

The potential large-scale energy benefit of EEB is in its production from a variety of feedstocks. In the aggregate, sources of inedible organic material including WWTP biosolids,

agricultural crop residues, organic municipal solid waste, and livestock manure represent several billion tonnes of potential EEB production feedstocks [39-42]. Crops dedicated to energy production are potential feedstocks; however, agricultural-based biofuel production has implicit limitations [43]. Energy crops that are ecologically low impact and yet produce high yields of feedstock were proposed to mitigate these limitations [44]. Moreover, coastal conservation approaches that include energy crop production add acreage to the fuel crop production portfolio while mitigating erosion and providing a barrier for storm protection. Key features of our overall biofuel production approach are that a variety of feedstocks were shown to be substrates for acidogenesis [17-20], and acidogenesis funnels complex feedstocks into a simplified platform for chemical and fuel production [18]. Indeed, PHA production with mixed microbial communities using SCFAs has been shown [22]. However, technical advancements such as process intensification of both biologic and chemical unit operations are needed to drive production costs lower. Thus, the scientific groundwork for rapid and widespread implementation of an EEB production industry is established, and the engineering efforts to integrate and commercialize this technology are needed.

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[Figure captions]

Fig. 1. Engine performance profiles for ULSD and EEB-ULSD blends. (a) exhaust temperature, (b) mean effective pressure (IMEP), (c) crank angle coefficient of variation, (d) start of combustion crank angle, (e) crank angle at 50% fuel burn (MFB-50), (f) peak cylinder temperature, (g) crank angle delta between 10% and 90% fuel burn (CA10-90), and (h) indicated power of a test engine fueled with different blends of EEB and ULSD. The test engine was run with 100% ULSD (dark blue line with arrow) as well as 5% (black, solid line and squares), 10% (orange line and diamonds), 20% (yellow line and triangles), 30% (light blue line and inverted triangles), and 50% (black, dashed line and arrows) volumetric mixtures of EEB and ULSD. Means with standard deviations are presented for engine tests with 100% ULSD ($n = 3$) that were run in conjunction with this EEB-ULSD study.

Fig. 2. Comparison of ULSD and EEB-ULSD blends impact on engine performance. Engine performance metrics were IMEP, crank angle coefficient of variation (COV), start of combustion (SOC), MGB-50, CA10-90, and indicated power (IP). EEB-ULSD blends were 5% (black bar), 10% (left-hatched bar), 20% (white bar), and 30% (right-hatched bar) volumetric mixtures of EEB and ULSD. (a) The percent changes under low load conditions. (b) The percent changes under high load conditions. Mean data with standard deviations are presented. An asterisk over a bar indicates a significant difference (Tukey's post-hoc test of ANOVA with 95% confidence intervals) between the EEB-ULSD blend and ULSD for that engine performance metric.

[Figure captions, continued]

Fig. 3. Fuel consumption and efficiency profiles for ULSD and EEB-ULSD blends. (a) fuel consumption (ISFC), (b) volumetric efficiency, and (c) thermal efficiency of a test engine fueled with different blends of EEB and ULSD. Lines and symbols are as described in Fig. 1. Means with standard deviations are presented for engine tests with 100% ULSD ($n=3$) that were run in conjunction with this EEB-ULSD study.

Fig. 4. Comparison of ULSD and EEB-ULSD blends for fuel consumption (ISFC) and emissions (CO, CO₂, NO_x, THC, and PM). EEB-ULSD blends were 5% (black bar), 10% (left-hatched bar), 20% (white bar), and 30% (right-hatched bar) volumetric mixtures of EEB and ULSD. (a) The percent changes under low load conditions. (b) The percent changes under high load conditions. Mean data with standard deviations are presented. An asterisk over a bar indicates a significant difference (Tukey's post-hoc test of ANOVA with 95% confidence intervals) between the EEB-ULSD blend and ULSD for that fuel characteristic.

Fig. 5. Emissions profiles for ULSD and EEB-ULSD blends. (a) NO_x, (b) CO, (c) PM, (d) THC, (e) CO₂, and (f) O₂ emissions of a test engine fueled with different blends of EEB and ULSD. Lines and symbols are as described in Fig. 1. Means with standard deviations are presented for engine tests with 100% ULSD ($n=3$) that were run in conjunction with this EEB-ULSD study.

Table 1 Summary of p-values obtained with ANOVA.

Measurement	p-value			
	EEB20-LL	EEB20-HL	EEB30-LL	EEB30-HL
IMEP			0.0212	0.0001
SOC	0.0390			< 0.0001
CA10-90	0.0286	0.0027	0.0362	< 0.00001
IP			0.0212	0.0001
CO ₂		0.0018	0.0212	< 0.0001
NO _x			0.0213	0.0443
PM			0.0464	0.0004

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 1-BW

Figure 3-BW

Figure 5-BW