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Ethyl 3-ethoxybutyrate, a new component of the transportation renewable fuel portfolio

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HIGHLIGHTS

- We characterize a novel fuel oxygenate, ethyl 3-ethoxybutyrate (EEB).
- EEB–diesel blends had cetane values that exceeded 40.
- Reduced criteria pollutant emissions was achieved with 5% and 10% EEB–diesel blends.
- Economically viable production of EEB at wastewater treatment plants is promising.
- EEB in the transportation fuel portfolio could lower global fossil carbon emissions.

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ABSTRACT

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

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

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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 (NOx) 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 517 cc 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 NOx 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 $m^3\ d^{-1}$ 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 h 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 h 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 517 cc 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%,

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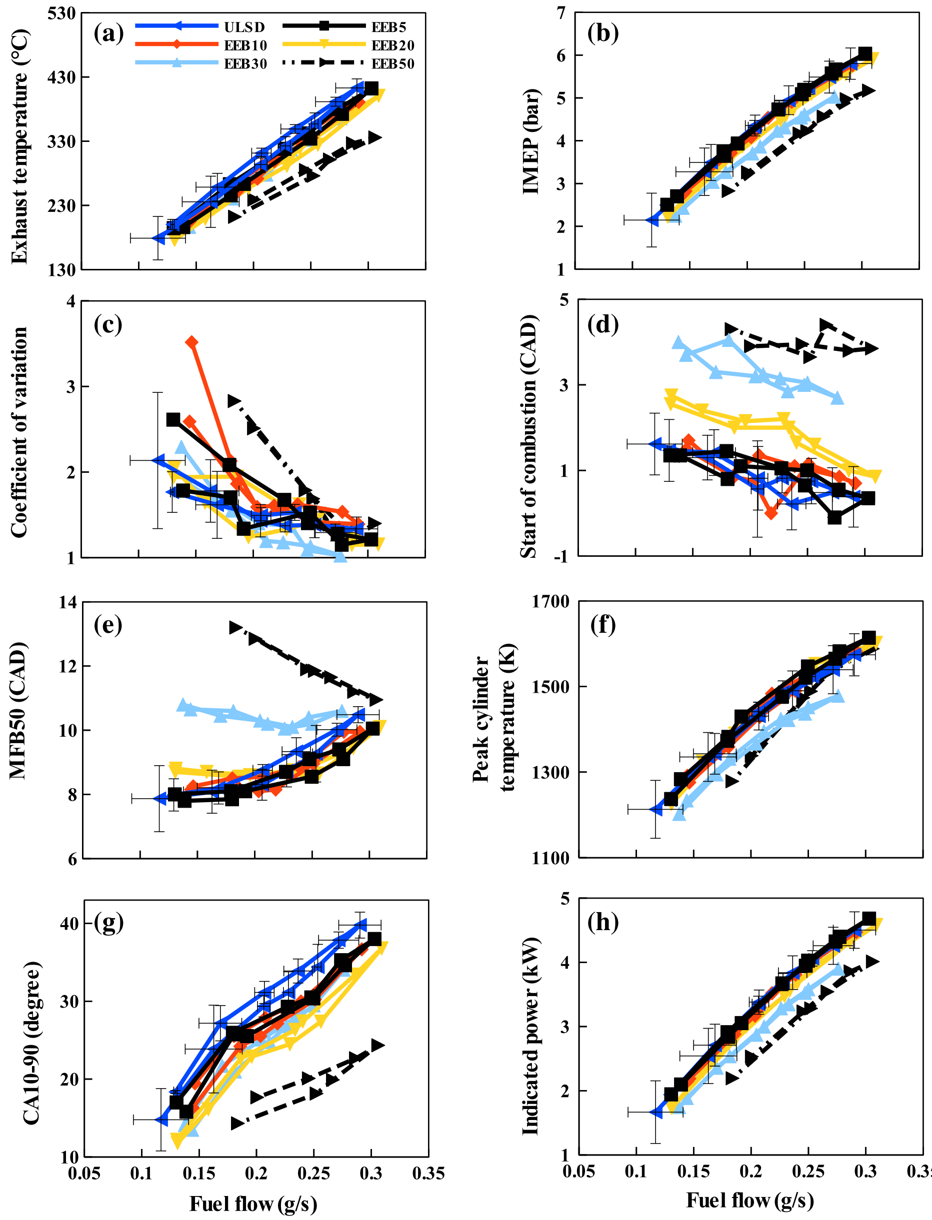

Fig. 1. Engine performance profiles for ULSD and EEB–ULSD blends. (a) Exhaust temperature, (b) mean effective pressure (IMEP), (c) crank angle coefficient of variation, (d) start of combustion crank angle, (e) crank angle at 50% fuel burn (MFB-50), (f) peak cylinder temperature, (g) crank angle delta 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. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.).

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 pronounce 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

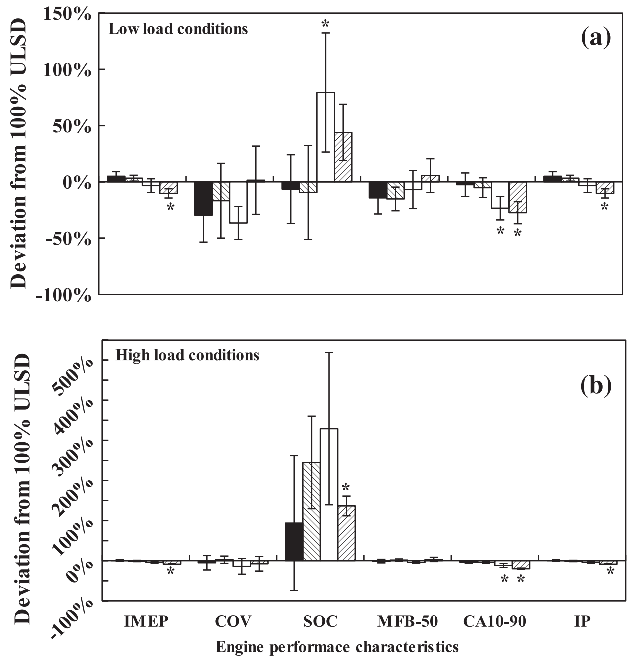

Fig. 2. Comparison of ULSD and EEB–ULSD blends impact on engine performance. Engine performance metrics were IMEP, crank angle coefficient of variation (COV), start of combustion (SOC), MGB-50, CA10-90, and indicated power (IP). EEB–ULSD blends were 5% (black bar), 10% (left-hatched bar), 20% (white 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.

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 NOx) and exhaust gases (i.e., O_2, HC, and CO_2) 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 where as CO and HC generally increased with increasing amounts of EEB in the fuel (Fig. 3). Oxygen, CO_2 and NOx 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, NOx, and carbon dioxide (CO_2) compared to ULSD (Table 1). Similar results occurred under high-load conditions; and again, the 30% blend produced significantly less PM, NOx, and CO_2 compared to ULSD. Otherwise, emissions data for EEB-diesel blends were statistically equivalent to ULSD, except the 20% blend produced significantly less CO_2 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.

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
NOx			0.0213	0.0443
PM			0.0464	0.0004

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

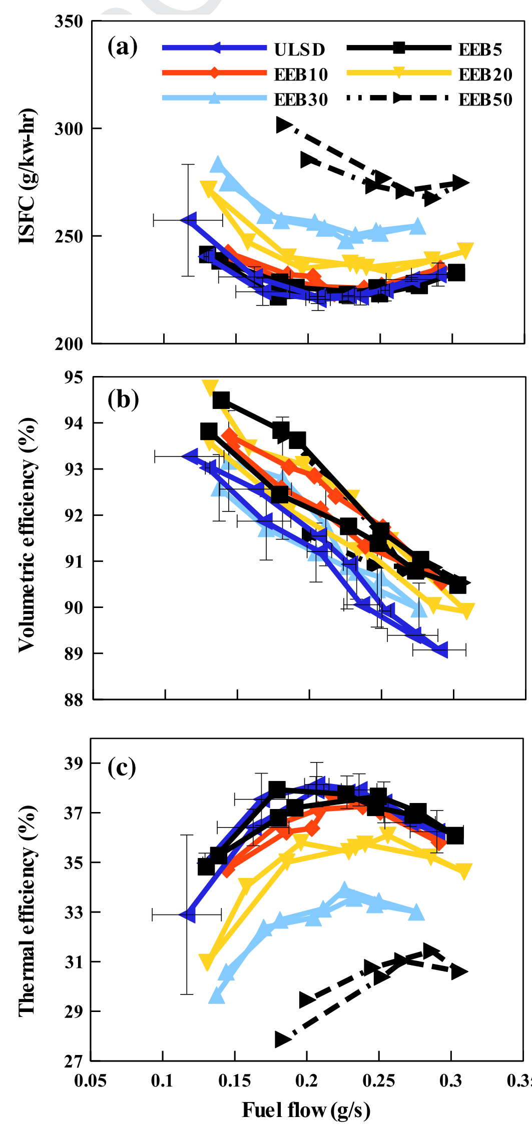

Fig. 3. Fuel consumption and efficiency profiles for ULSD and EEB–ULSD blends. (a) Fuel consumption (ISFC), (b) volumetric efficiency, and (c) thermal efficiency of a test engine fueled with different blends of EEB and ULSD. Lines and symbols are as described in Fig. 1. Means with standard deviations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

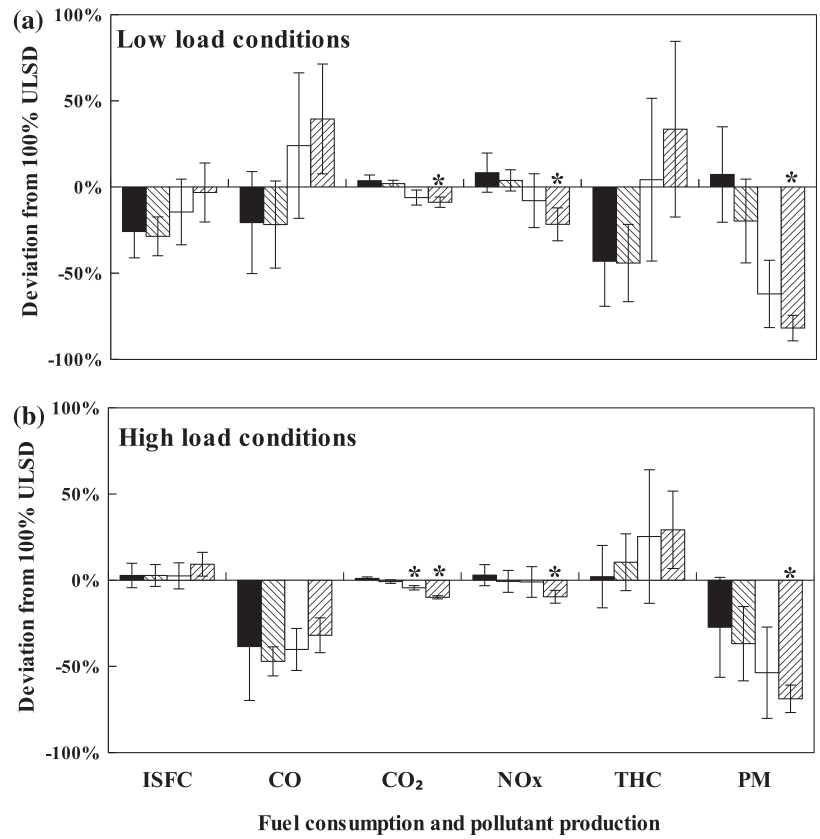

Fig. 4. Comparison of ULSD and EEB–ULSD blends for fuel consumption (ISFC) and emissions (CO, CO_2, NOx, THC, and PM). EEB–ULSD blends were 5% (black bar), 10% (left-hatched bar), 20% (white bar), and 30% (right-hatched bar) volumetric mixtures of EEB and ULSD. (a) The percent changes under low load 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.

biosolids fermentation and that the homopolymer, PHB, was accumulated in a separate unit operation. The model output under these conditions was 1117 kg acetate/h, 75 kg volatile suspended solids/h, and 323,745 kg water/h for biosolids fermentation, which in turn resulted in predicted polymer production outputs of 360 kg PHB/h, 1813 kg volatile suspended solids/h, and 8694 kg water/h. 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 NOx occurred with higher blend levels and EEB co-blended with biodiesel might serve to mitigate elevated NOx production associated with unsaturated biodiesel. Indeed, the ethoxy moiety may be the source of NOx 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

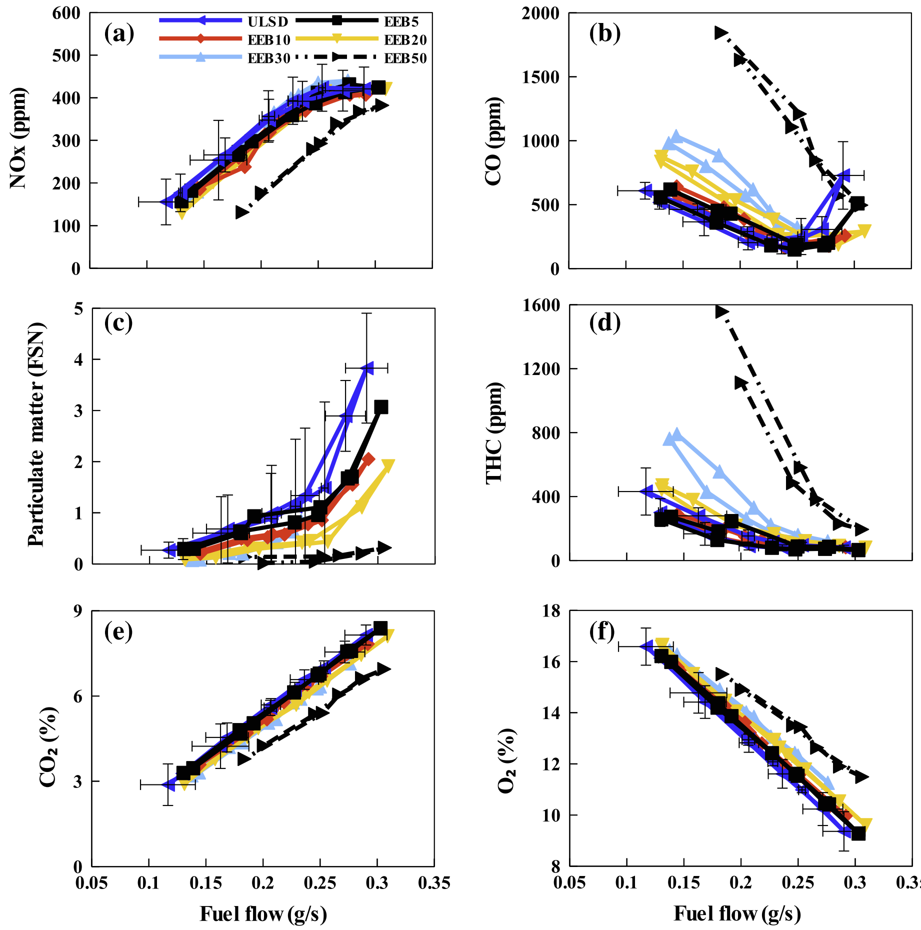

Fig. 5. Emissions profiles for ULSD and EEB–ULSD blends. (a) NOx, (b) CO, (c) PM, (d) THC, (e) CO_2, and (f) O_2 emissions of a test engine fueled with different blends of EEB and ULSD. Lines and symbols are as described in Fig. 1. Means with standard deviations are presented for engine tests with 100% ULSD ($n = 3$) that were run in conjunction with this EEB–ULSD study.

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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References

[1] Panel on Alternative Liquid Transportation Fuels (PALTF). Liquid transportation fuels from coal and biomass: technological status, costs, and environmental impacts. Washington, D.C.: The National Academies Press; 2009.
[2] Davis SJ, Caldeira K, Matthews HD. Future CO_2 emissions and climate change from existing energy infrastructure. Science 2010;329:1330–3.
[3] O'Sullivan J. Liquid fuel. In: International energy outlook. Washington, D.C.: U. S. Energy Information Administration; 2011. p. 25–41.
[4] Atabani AE, Silitonga AS, Badruddin IA, Mahlia TMI, Masjuki HH, Mekhilef S. A comprehensive review on biodiesel as an alternative energy resource and its characteristics. Renew Sust Energy Rev 2012;16:2070–93.
[5] Xue J, Grift TE, Hansen AC. Effect of biodiesel on engine performances and emissions. Renew Sust Energy Rev 2011;15:1098–116.
[6] Tsai J-H, Chen S-J, Huang K-L, Lin W-Y, Lee W-J, Lin C-C, et al. Emissions from a generator fueled by blends of diesel, biodiesel, acetone, and isopropyl alcohol: analyses of emitted PM, particulate carbon, and PAHs. Sci Total Environ 2014;466–467:195–202.
[7] Chang Y-C, Lee W-J, Wu TS, Wu C-Y, Chen S-J. Use of water containing acetone–butanol–ethanol for NO_x-PM (nitrogen oxide-particulate matter) trade-off in the diesel engine fueled with biodiesel. Energy 2014;64:678–87.
[8] Weber de Menezes E, da Silva R, Cataluna R, Ortega RJC. Effect of ethers and ether/ethanol additives on the physicochemical properties of diesel fuel and on engine tests. Fuel 2006;85:815–22.
[9] Storey JME, Bunce MP, Edmonds JW, Findlay RH, Ritchie SMC, Eyers L, et al. Fuel economy and pollutant emissions from an automobile fueled with ethyl 3-ethoxybutyrate and gasoline. Fuel 2015 [submitted for publication].
[10] Mohrig JR, Fu SS, King RW, Warnet R, Gustafson G. Stereochemistry of nucleophilic conjugate addition. Addition of ethanol-*d* and 2-methyl-2-propanethiol-*d* to ethyl crotonate. J Am Chem Soc 1990;112:3665–7.
[11] Mohrig JR, Lee PK, Stein KA, Mitton MJ, Rosenberg RE. Diastereoselectivity in the protonation of ester enolates. The importance of aggregation with LDA. J Org Chem 1995;60:3529–32.
[12] Mohrig JR, Rosenberg RE, Apostol JW, Bastienaansen M, Evans JW, Franklin SJ, et al. Diastereoselectivity of enolate anion protonation. H/D exchange of β-substituted ethyl butanoates in ethanol-*d*. J Am Chem Soc 2007;119:479–86.

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[13] Caballero A, Dıaz-Requejo MM, Belderraın TR, Nicasio MC, Trofimenko S, Perez PJ. Functionalization of carbon–hydrogen bonds of hydrocarbons and ethers via carbene insertion with copper(I)-homoscorpionate catalysts. Organometallics 2003;22:4145–50.
[14] Zhang X, Luo R, Wang Z, Deng Y, Chen G-Q. Application of (R)-3-hydroxyalkanoate methyl esters derived from microbial polyhydroxyalkanoates as novel biofuels. Biomacromolecules 2009;10:707–11.
[15] Wang SY, Wang Z, Liu MM, Xu Y, Zhang XJ, Chen G-Q. Properties of a new gasoline oxygenate blend component: 3-hydroxybutyrate methyl ester produced from bacterial poly-3-hydroxybutyrate. Biomass Bioenergy 2010;34:1216–22.
[16] McMurry ZA, Smoot JC. Process for producing a renewable biofuel from waste water treatment plants. U.S. Patent No. 8,377,151; 2013.
[17] Lee WS, Chua ASM, Yeoh HK, Ngoh GC. A review of the production and applications of waste-derived volatile fatty acids. Chem Eng J 2014;235:83.
[18] Chang HN, Kim N-J, Kang J, Jeong CM. Biomass-derived volatile fatty acid platform for fuels and chemicals. Biotechnol Bioprocess Eng 2010;15:1–10.
[19] Agbogbo FK, Holtzapple MT. Fixed-bed fermentation of rice straw and chicken manure using a mixed culture of marine mesophilic microorganisms. Bioresour Technol 2007;98:1586–95.
[20] Thanakoses P, Black AS, Holtzapple MT. Fermentation of corn stover to carboxylic acids. Biotechnol Bioeng 2003;83:191–200.
[21] Yuan H, Chen Y, Zhang H, Jiang S, Zhou Q, Gu G. Improved bioproduction of short-chain fatty acids (SCFAs) from excess sludge under alkaline conditions. Environ Sci Technol 2006;40:2025–9.
[22] Serafim LS, Lemos PC, Albuquerque MGE, Reis MAM. Strategies for PHA production by mixed cultures and renewable waste materials. Appl Microbiol Biotechnol 2008;81:615–28.
[23] Bunting B, Bunce M, Joyce B, Crawford R. Investigation and optimization of biodiesel chemistry for HCCI combustion. In: Steve Hung S, Subic A, Wellnitz J, editors. Sustainable automotive technologies. Berlin, Heidelberg: Springer-Verlag; 2011. p. 51–8.
[24] Bunting BG, Bunce M, Puduppakkam K, Naik C. Kinetic modeling of fuel effects over a wide range of chemistry, properties, and sources. In: Subic A, Wellnitz J, Leary M, Koopmans L, editors. Sustainable automotive technologies. Berlin, Heidelberg: Springer-Verlag; 2012. p. 127–33.
[25] Bunce M, Bunting BG, Wang J, Crawford R. Experimental and statistical comparison of engine response as a function of fuel chemistry and properties in CI and HCCI engines. SAE Technical Paper 2012-01-0857 2012, http://dx.doi.org/10.4271/2012-01-0857.
[26] Satoh H, Iwamoto Y, Mino T, Matsuo T. Activated sludge as a possible source of biodegradable plastic. Water Sci Technol 1998;38:103–9.
[27] Choi J, Lee SY. Efficient and economical recovery of poly(3-hydroxybutyrate) from recombinant *Escherichia coli* by simple digestion with chemicals. Biotechnol Bioeng 1999;62:546–53.
[28] Coats ER, Loge FJ, Wolcott MP, Englund K, McDonald AG. Synthesis of polyhydroxyalkanoates in municipal wastewater treatment. Water Environ Res 2007;79:2396–403.
[29] Cui Z, Beach ES, Anastas PT. Green chemistry in China. Pure Appl Chem 2011;83:1379–90.
[30] Bergeron SR. Chartering and operations. In: Huber M, editor. Tanker operations a handbook for the person-in-charge. Centreville: Cornell Maritime Press; 2001. p. 210–28.
[31] Lapuerta M, Armas O, Rodríguez-Fernández J. Effect of biodiesel fuels on diesel engine emissions. Prog Energy Combust Sci 2008;34:198–223.
[32] Hajbabaei M, Johnson KC, Okamoto RA, Mitchell A, Pullman M, Durbin TD. Evaluation of the impacts of biodiesel and second generation biofuels on NO_x emissions for CARB diesel fuels. Environ Sci Technol 2012;46:9163–73.
[33] Hajbabaei M, Johnson KC, Okamoto RA, Durbin TD. Evaluation of the impacts of biofuels on emissions for a California certified diesel fuel from heavy-duty engines. SAE Int J Fuels Lubr 2013;6:393–406.
[34] Wang X, Zhan Z, Hu T, Huang Z. Influence of biodiesel/diesel blends on particulate emissions in a turbocharged common rail diesel engine. SAE Int J Fuels Lubr 2014;7:643–52.
[35] Bari S. Performance, combustion and emission tests of a metro-bus running on biodiesel-ULSD blended (B20) fuel. Appl Energy 2014;124:35–43.
[36] Pugazhvadivu M, Rajagopan S. Investigations on a diesel engine fueled with biodiesel blends and diethyl ether as an additive. Indian J Sci Technol 2009;2:31–5.
[37] Kannan TK, Marappan R. Comparative study of performance and emission characteristics of a diesel engine fueled by emulsified biodiesel/diethyl ether blended biodiesel. J Appl Sci 2011;16:2961–7.
[38] Qi DH, Chen H, Geng LM, Bian YZ. Effect of diethyl ether and ethanol additives on the combustion and emission characteristics of biodiesel–diesel blended fuel engine. Renew Energy 2011;36:1252–8.
[39] Beecher N. USA, Summary of wastewater treatment solids management in the United States. In: LeBlanc RJ, Matthews P, Richard RP, editors. Global atlas of excreta, wastewater sludge, and biosolids management: moving forward the sustainable and welcome uses of a global resource. Nairobi: United Nations Human Settlements Programme; 2008. p. 542–8.
[40] Industry and Economics International Environmental Technology Centre (IEIETC). Integrated solid waste management plan training manual. Assessment of current waste management system and gaps therein, vol. 2. Osaka: United Nations Environmental Programme; 2009.
[41] Foley JA, Ramankutty N, Brauman KA, Cassidy ES, Gerber JS, Johnston M, et al. Solutions for a cultivated planet. Nature 2011;478:337–42.
[42] Pelletier N, Tyedmers P. Forecasting potential global environmental costs of livestock production 2000–2050. Proc Natl Acad Sci USA 2010;107:18371–4.
[43] Karp A, Richter GM. Meeting the challenge of food and energy security. J Exp Bot 2011;62:3263–71.
[44] Tilman D, Hill J, Lehman C. Carbon-negative biofuels from low-input high-diversity grassland biomass. Science 2006;314:1598–600.