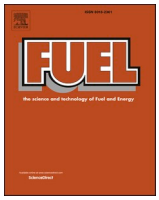
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Full Length Article



Potential economic values of low-vapor-pressure gasoline-range bio-blendstocks: Property estimation and blending optimization

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ABSTRACT

Adding bio-blendstock into gasoline can reduce greenhouse gas emissions and potentially enhance fuel properties and boost engine efficiencies. A competitive bio-blendstock should have lower prices and/or superior properties. Gasoline is specified by final blended properties rather than compositions, while adding bio-blendstocks, most likely oxygenates, will modify the property mixing rules due to the non-ideal interactions between polar and nonpolar components. This paper presents an equation-of-state model for predicting Reid vapor pressure, non-linear blending models for computing key properties of final products, and an optimization approach to identify key economic drivers. Those models are used to estimate the potential economic value of bio-blendstocks, which is presented by its calculated break-even value as a feedstock to petroleum refineries for gasoline blending without any government subsidy or renewable tax credit. In additional to ethanol, six low-vapor-pressure bio-blendstock candidates were evaluated: i-propanol, n-propanol, i-butanol, diisobutylene, cyclopentanone, and a mixture of furans. Reid vapor pressure, distillation temperatures, and octane numbers were identified as the key economic drivers of adding bio-blendstock to a petroleum-derived base fuel. The calculated economic value ranks as furan mixture (4.9) > cyclopentanone > *n*-propanol ≈ *iso*-propanol > *iso*-butanol > diisobutylene (2.4) in US dollar per gasoline gallon equivalent ($/gge) in 2013 to 2017 5-year averaged price basis. The bio-blendstocks with higher octane numbers may have higher potential economic values. The uncertainties in property predictions may lead to roughly 15% deviation in the potential economic value.

1. Introduction

Biofuels are synthetic fuels generated from biomass and waste streams that can be directly upgraded into transportation fuels such as gasoline, diesel, and jet fuel [1–3]. Biofuels may increase domestic production of energy, reduce life-cycle CO_2 emission and offer advantages in engine performance compared with petroleum-derived fuels. Compared with conventional fuels, biofuels may have a significant concentration of oxygenates depending on the conversion pathway used [2,4,5]. Technologies to convert all those oxygenates into hydrocarbons to satisfy fuel specifications are available but may be currently uneconomical [6] and have associated product yield loss with deoxygenation. An alternative approach is to produce bio-blendstocks that can be blended with conventional fuels and have the potential to boost both fuel properties and engine performance [4,7]. Blending biomass-derived ethanol into the gasoline pool is a successful example of this approach as ethanol has a relatively high octane number and can be easily derived from sugars or starch [8]. However, adding ethanol also increases the Reid vapor pressure (RVP) of gasoline [9] and consequently reduces the blending volume of low-cost butanes into the gasoline pool [10,11]. Considering low-vapor-pressure bio-blendstocks that also have high octane numbers may allow more lower-cost components to be added to the gasoline pool (e.g., butane, light straight run naphtha, isomerate) and/or reduce the demands on high-cost components (e.g., alkylate and

Abbreviations: AKI, antiknock index; ASTM, American Society of Testing and Materials; BEV, Break-even value; EIA, U.S. Energy Information Administration; CBOB, conventional blendstock for oxygenate blending; CARBOB, California reformulated blendstock for oxygenate blending; CPA, Cubic Plus Association; EN, Engineering Standards; EOS, equation of state; LP, linear programming; MFSP, Minimum fuel selling price; MON, motor octane number; PIMS, Process Industry Modeling System; R&D, Research and development; RBOB, reformulated blendstock for oxygenate blending; RFG, reformulated gasoline; RON, research octane number; RVP, Reid vapor pressure; S, Octane sensitivity.

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reformate), which may have the potential to improve the economics of a petroleum refinery. On the other hand, if the vapor pressure is too low, other volatility constraints might be violated [12], such as cold-start and drivability. Selecting and determining blending fractions of blendstocks is a complicated optimization problem with numerous constraints. The focus of this work is to identify the key physical property constraints of gasoline that drive economics, characterize and estimate key physical properties (Reid vapor pressure, distillation curve and octane numbers), and determine the potential economic value of gasoline-range low-vapor-pressure bio-blendstocks to petroleum refiners.

Conventional gasoline is a petroleum-derived liquid fuel consisting of hundreds of hydrocarbons, enhanced with additives and blending agents. Essentially, it is a substitutable commodity with a large market and specified by properties rather than chemical compositions. The fraction of each blendstock in the finished gasoline products must be carefully optimized to satisfy all regulations and quality specifications as well as be economical to the refiner/blender. Of all characteristics constrained in gasoline across the world, antiknock performance and volatility are the two most important characteristics for vehicle drivability [13]. Research octane number (RON) and motor octane number (MON) are the two key measures for antiknock performance [14]. The difference between RON and MON is octane sensitivity, while the average of RON and MON is called road octane number or antiknock index (AKI). For the United States market, gasoline is graded by AKI while other countries use RON instead [15]. For gasoline volatility, ASTM D4814 [12], developed by ASTM International, and EN 228, developed by European Committee for Standardization, are the most widely used standards [13]. ASTM D4814 sets constraints on vapor pressure and distillation temperature at 10 vol%, 50 vol%, and 90 vol% evaporated (T10, T50, and T90) [12]. EN 228 sets constraints on vapor pressure and volume percentage off at 70 °C, 100 °C, and 150 °C (E70, E100, and E150). Vapor pressure is the most important property for cold-start and warm-up drivability. The front-end volatility (i.e., T10, E70) is important for easy cold and hot starting, and hot fuel handling. The midrange volatility (i.e., T50, E100) is important for rapid warm up and smooth running, good short-trip fuel economy, and protection against carburetor icing and hot stalling. The tail-end volatility (i.e., T90, E150) is important for good fuel economy after engine warm up and minimal volatile organic compound emissions [12,16].

Several techno-economic analyses have been conducted to evaluate the production cost and the minimum fuel selling price (MFSP) of biofuels and/or bio-blendstocks over the past decade [5,6,17,18]. However, few works have been conducted to analyze the impact of introducing biofuels and/or bio-blendstocks into fuel markets from the perspectives of fuel properties driven by engine performance and economic benefits. As mentioned, adding bio-blendstocks into gasoline will change both the properties and formula of gasoline. The potential economic value of bio-blendstocks to petroleum refiners can be determined by comparing the balance of streams within the refinery before and after adding bio-blendstocks with its potential relative impact on economics [19]. In a petroleum refinery, its economics is usually maximized on a regular basis by solving the refinery linear programming (LP) planning problem to determine the type and amount of crude oil purchase and product sale [20]. This refinery LP problem is subject to numerous constraints on supplies, demands, properties, etc. Aspen Process Industry Modeling System (PIMS) is one of the most widely used and reliable software to solve this problem [19]. However, a full-scale refinery LP planning model, from crude oil purchasing to fuel and co-product selling, requires extensive and detailed information and process data, such as crude oil assays, material and energy balance of each separation, and conversion steps at different operating conditions and feed properties, which are generally unavailable to the public and require intensive effort to obtain. Therefore, there are very few studies in literature that discuss refinery optimization and its operational economics. To simplify the problem and to develop an alternative approach mostly based on open-source data, blending optimization was performed in this work, including blendstock purchase, blending, and finished fuel sale. We believe that such an analysis, even though somewhat simplistic, is valuable to the research community of bioenergy technologies for comparing bio-blendstock candidates and identifying opportunities for refinery integration. This analysis was conducted to evaluate the potential economic value of bio-blendstock candidates and to obtain the optimal economics and use of resources subjected to property constraints on final gasoline products given the cost, supplies, demands, and properties of each blendstock and product. The blending model used in this work can also be embedded into full refinery LP models of petroleum refineries with different configurations for more rigorous analyses. Note that component properties and prices are the core of gasoline blending optimization.

One challenge of the simplified approach is to estimate the delivered prices of petroleum-based blendstocks that will be used in the model because they are not directly available in the market for sale. A method recommended by S&P Global Platts can be applied to approximate the prices of those gasoline-range, petroleum-based blendstocks by the incremental value of octane number [21]. Another challenge comes from the nonlinearities in property blending rules. While the property blending rules of hydrocarbons, typically petroleum derived, are well understood and most likely can be approximated by linear models [15], the addition of bio-blendstocks may significantly change the property blending rules due to the non-ideal interactions between nonpolar (i.e., hydrocarbons) and polar (i.e., oxygenates) compounds [4]. Some of the widely used linear property blending models may no longer be valid due to the present of oxygenates in the system, especially for octane numbers and volatility measures [13].

In order to have a reasonable estimate on fuel properties, it is critical to have experimental measurements and appropriate property blending rules. McCormick et al. [22,23] measured the RON and octane sensitivity of a variety of oxygenates blended in two commercial gasoline blends, reformulated blendstock for oxygenate blending (RBOB) and conventional blendstock for oxygenate blending (CBOB). It was observed that strong non-linear blending behavior existed at low oxygenate concentrations, as previously reported by others [24]. Other than octane numbers, the non-linear blending behavior also exists when predicting mixtures' vapor pressure and distillation curve (i.e., T10, T50, and T90) [23,25]. As observed by McCormick et al. [23], at low blend level (10 vol%), the effects of bio-blendstocks on the distillation curve are modest, except for ethanol, methanol, and methyl acetate, which depress the front end of the distillation curve. At a blend level above 20 vol%, significant changes in T50 were observed for most of the investigated bio-blendstocks. Andersen et al. [25] indicated that most alcohol-gasoline mixtures exhibit near-azeotropic behavior that significantly affects the shape of distillation curves and reported a similar shape of distillation curves as McCormick et al. [23]. Gaspar et al. [4] reviewed a few methods to measure and predict the vapor pressure of gasoline containing oxygenates. In the work, a reliable approach was developed in Aspen Plus to predict RVP of bio-blendstocks and gasoline mixtures. The Cubic Plus Association (CPA) equation of state (EOS) was identified as the preferred property model able to estimate RVP of all binary and ternary mixtures of a California reformulated blendstock for oxygenate blending (CARBOB) and oxygenates. However, this model is too complicated to be applied to blending optimization, especially to full-scale refinery modeling [26,27]. A surrogate blending model, which is simpler but can still represent the non-linear blending behavior is needed for optimization and assessment of the potential economic value of new blendstocks [19].

Beyond doubt, the potential economic values of bio-blendstocks evaluated via blending optimization are subjected to various sources of uncertainties, such as property measures and estimation, and fluctuating prices of crude oil leading to volatile economics for gasoline products. For example, the EOS-based RVP prediction method using only built-in database information in Aspen Plus may introduce 10% uncertainties even when the best EOS is selected [4]. Uncertainty can

also be introduced when reducing the rigorous property prediction model into a relatively simple surrogate model suitable for blending optimization, and when using experimental data to fit a linear or non-linear property blending model as a result of data fitting. Moreover, the potential economic value of bio-blendstocks by this method are strongly correlated to market wholesale gasoline prices, which are affected by the level of supply and demand as well as crude oil prices. For example, the U.S. total gasoline wholesale price ranged from $1.05 to $3.17 per gallon over the last 10 years [28].

With the above considerations in mind, blending optimization was conducted to estimate the potential economic value of new bio-blendstocks to petroleum refineries due to their superior properties. Simple non-linear property blending models were developed based on experimental measures and rigorous property models for key properties. Uncertainties regarding property measures and estimations, as well as market prices of gasoline products, were quantified by sensitivity studies. This analysis is aimed to (1) identify the key fuel properties that drive the economic values of bio-blendstocks for a petroleum refinery, (2) guide future research and development (R&D) on finding new bio-blendstock candidates based on fuel properties, and (3) recommend a potential price target for bioenergy technologies under development. The methodology developed in this study can be widely applied to other bio-blendstocks outside the few considered here.

2. Method

The U.S. Energy Information Administration (EIA) estimates that the total fuel ethanol consumption in the United States was equal to about 10% of the total volume of finished motor gasoline consumption in 2019 [28]. In this study, potential economic values and their uncertainties were analyzed for six bio-blendstock candidates: cyclopentanone, *iso*-butanol, *n*-propanol, furan mixture, diisobutylene, and *iso*-propanol, in an ethanol-free environment (E0) or a 10 vol% ethanol in gasoline environment (E10). Those bio-blendstock candidates were selected from the Top Ten Bio-blendstock Report for Gasoline Engines, where more than 400 blendstocks were evaluated based on their potential to deliver the highest engine efficiency, and potential practical barriers [29]. Fig. 1 summarizes the proposed analysis approach, data inputs, assumptions (detailed in Section 2), and its potential applications in the bioenergy community and the transportation sector (detailed in Section 3).

2.1. Blending optimization

Aspen PIMS was used to conduct blending optimization and determine the potential economic value of bio-blendstock candidates from both property and economic perspectives. In Aspen PIMS, the user needs to define the supply and demand (capacity, costs feedstocks/blendstocks and prices of products), the blending information (property specifications of products, static properties of blendstocks, and blending models/formulas), and the refinery unit operation model (mass and energy balance and intermediate product properties). This work focuses on the impacts of blending bio-blendstocks into gasoline at the terminal. Therefore, refining crude oil to intermediate gasoline-range blendstocks is out of this scope. Only blendstock purchasing, product blending, and product sale were considered in this optimization.

As shown in Fig. 2, the objective of the blending optimization problem is to maximize economic measures (E), defined in Eq. (1), subject to inequality constraints on blendstock supply (Eq. (2)), product demands (Eq. (3)), product qualities/properties (Eq. (4)), and equality constraints on property mixing rule (Eq. (5)) and mass balance (Eqs. (6) and (7)). In these equations, p_p and v_p are the wholesale price and volume of product p; c_i and $v_i$are the estimated cost and volume of blendstock i; v_{ip} is the volume of blendstock i blended into product p; Q_p^k and $Q_i^k$are the property k of product$p$, and blendstock i, respectively; s_i^l, s_i^u, d_p^l, d_p^u, $Q_p^{k,l}$, $Q_p^{k,u}$ are the lower (l) and upper limits (u) of blendstock supplies (s), product demands (d), and product qualities/properties (Q_p^k), respectively; and x_{ip} is the volume fraction of bio-blendstock i in product p, as defined in Eq. (8).

$$\text{Maximize} \quad E = \sum_p p_p v_p - \sum_i c_i v_i \tag{1}$$

$$\text{Subject to} \quad s_i^l \le v_i \le s_i^u \tag{2}$$

$$d_p^l \le v_p \le d_p^u \tag{3}$$

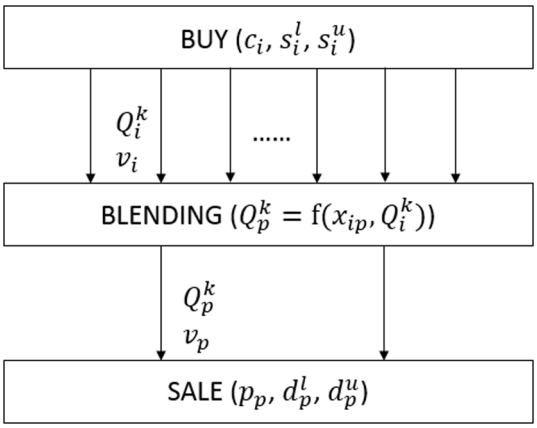


Fig. 2. Schematic diagram of blending optimization approach used in this paper.

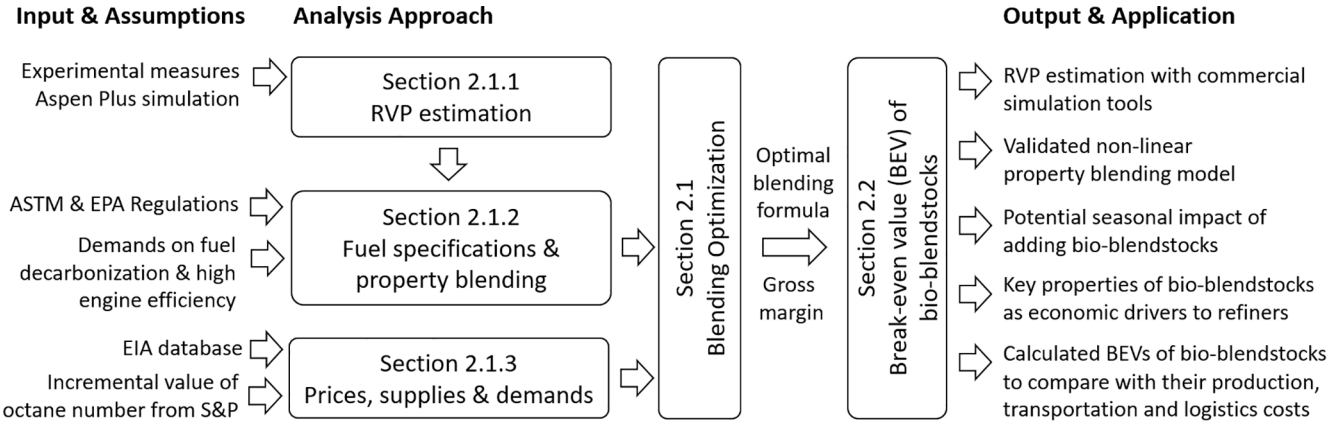


Fig. 1. Proposed analysis approach and its potential application.

$$Q_p^{k,l} \le Q_p^k \le Q_p^{k,u} \tag{4}$$

$$Q_p^k = f\left(x_{ip}, Q_i^k\right) \tag{5}$$

$$v_i = \sum_p v_{ip} \tag{6}$$

$$v_p = \sum_i v_{ip} \tag{7}$$

$$x_{ip} = v_{ip}/v_p \tag{8}$$

2.1.1. Vapor pressure estimation

In our previous study [4], a flowsheet model was developed in Aspen Plus to estimate the vapor pressure of non-oxygenated gasoline (also called blendstock for oxygenate blending or BOB) and oxygenated (i.e. reformulated) gasoline, and at different blending levels. In the model, a blend of 122 model compounds were used to meet the bulk properties such as boiling range, density, and aromatic content of a commercial CARBOB, gasoline blend used in the laboratory experiment, provided by Intertek, Inc. The model components were selected based on the results of detailed hydrocarbon analysis according to ASTM D6730 and the availability in Aspen Property Database. In the flowsheet as shown in Fig. 3, the user-defined CARBOB stream was mixed with another user-defined oxygenate mixture at a desired blend level and then sent to a flash drum. To match the standard measurement procedure of RVP (ASTM 5191), a design spec was set up in Aspen Plus to adjust the pressure of the flash drum until the volumetric flow of the vapor stream was four times the volumetric flow of the liquid stream at 37.8 °C (100°F). The final pressure of the flash drum was the RVP by definition. This method was also applied to estimate the RVP of gasoline blended with the bio-blendstock candidates of interest in this study. Model validation was conducted by comparing the simulation results with a large set of experimental measures of CARBOB blended with 10, 20 and 30 vol% oxygenates, including some newly measured RVP data. More details about the experimental procedure, modeling approach, and model validation against preliminary experimental data can be found in Gaspar et al. [4].

2.1.2. Properties, specifications, and property models

As shown in Eq. (4) and Table 1, gasoline products have strict property specifications related to both volatility and compositions. The properties of the final product can be estimated given the properties of each blendstock (Q_i^k), the volume fraction (x_{ip}), and appropriate blending rules ($f\left(x_{ip}, Q_i^k\right)$). In the United States, the property specifications of gasoline vary both seasonally and geographically. Six volatility classes are specified in ASTM D4814 [12,30] for gasoline along with a seasonal and geographical schedule. EPA and local administrations have different RVP requirements. To reduce the complexity, the two extreme volatility classes (AA is the least volatile class and E is the most volatile class) from ASTM D4814 are selected in this work to represent the seasonal impacts of gasoline blending for all investigated bio-blendstocks. Sensitivity studies were conducted with *iso*-propanol for other volatility classes between the two extremes. Table 1 summarizes representative specifications ($Q_p^{k,l}$ and $Q_p^{k,u}$ defined in Eq. (4)) of reformulated gasolines in a potential future fuel market demanding fuel decarbonization and high engine efficiency [31]. Sources and assumptions are mentioned in the footnotes.

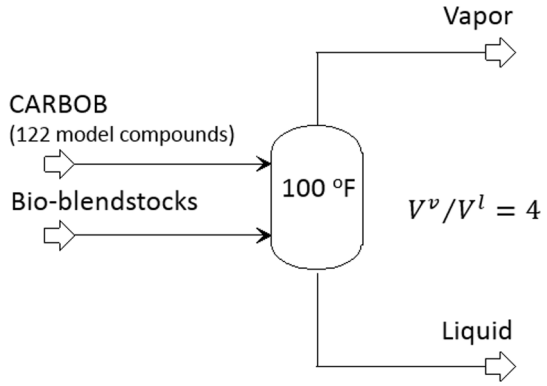


Fig. 3. Flowsheet developed to estimate RVP in Aspen Plus (V^v, V^l = vapor/liquid volumetric flowrate).

Table 1
Property specifications of the finished gasoline-oxygenate blend (for Eq. (4) in this work).

Volatility	Summer	Winter	Composition	All season
Representative volatility class (1)	AA	E	Anti-Knock Index (AKI) (2,3)	> 87 (Regular)>93 (Premium)
Specific gravity (2)	>0.7	>0.7	Octane sensitivity (3)	>8 (Regular)> 10 (Premium)
RVP (psi)	<7.8	<15	Sulfur (ppm, wt) (4)	<10
T10 (°F) (1)	<158	<122	Benzene (vol%) (5)	<0.6
T50 (°F) (1, 3)	150–250	150–230	Olefins (vol%) (2)	<25
T90 (°F) (1)	<374	<365	Aromatics (vol %) (2)	<50
			Oxygen (wt%) (2, 6)	<4

(1) Volatility classes were specified by ASTM D4814 [12,30]. T10, T50, and T90 are defined as the 10 vol%, 50 vol%, and 90 vol% evaporated temperatures, respectively. For gasoline before ethanol blending, the T50 minimum is 170 °F. A lower T50 minimum is specified for fuels containing 1–15 vol% ethanol than for solely non-oxygenated hydrocarbon fuels.
(2) These properties are not specified by nationwide standards or regulations in the United States, but are specified by EPA's complex model for emission performance, or often seen in pipeline and "internal" refinery gate specifications [32]. For different regions, products and fuel markets, the values provided in this table may be subject to change.
(3) Octane sensitivity = RON-MON. AKI = (RON + MON)/2. In the current fuel market, octane sensitivity is not specified. A high-octane sensitivity is desired by boosted spark-ignition engines [31], which may be required in a future market with lower carbon intensity fuels and high efficiency engines.
(4) The annual average gasoline sulfur content is specified by the EPA Tier 3 fuel program [12].
(5) The annual average gasoline benzene content is specified by the EPA Mobile Source Air Toxics rule [12].
(6) Currently, the oxygen limit varies with the EPA Substantially Similar Rule [12]. In the future, EPA waivers and additional regulations will be required to relax this constraint and therefore introduce bio-blendstocks at volume.

For petroleum-derived blendstocks, dominated by hydrocarbons, the linear blending rule as shown in Eq. (9) was used to predict the properties of final products (Q_p^k) in the refinery LP model for decades. When bio-blendstocks are added to the gasoline pool, Eq. (9) can still be applied to estimate properties unlikely being affected by the non-ideal interactions between polar and non-polar compounds, such as sulfur, olefins, aromatics, benzenes and oxygenates contents. Note that for sulfur and oxygenate contents, Eq. (9) is on weight basis rather than volume basis. However, the octane numbers, distillation curve (T10, T50, T90), and RVP can be affected by those non-ideal interactions [4,22–25]. For those properties, a non-linear blending rule can be used as shown in Eq. (10a). The RVP Index defined in Eq. (11) rather than RVP was used in Eq. (9) to calculate the RVP of final gasoline products based on the experience of the petroleum industry [15]. In Eqs. (9) and (10a), A_{ij}^k is the binary interaction parameter of property k between blendstocks i and j; Q_i^k is the volumetric equivalent property of blendstock i, which is the best property values that can be fit into the blending

rule to estimate the properties of final products. For simplification, it was assumed that for the same bio-blendstocks, its binary interaction between different hydrocarbon streams (listed in Table 2) were the same. When $A_{ij}^{k} \neq 0$, the volumetric equivalent blending property of bio-blendstocks (Q_b^k) can be approximated by Eq. (10b), where x_{bp} is its volume fraction in the product. In this study, Q_i^k was approximated by the neat component property of the each blendstock, as listed in Tables 2 and 3, except the RVP, T10, T50, T90, RON, and MON of bio-blendstocks.

$$Q_p^k = \sum x_{ip} Q_i^k \tag{9}$$

$$Q_p^k = \sum x_{ip} Q_i^k + \sum A_{ij}^k x_{ip} x_{jp} \tag{10a}$$

$$Q_b^k = Q_i^k|_{i=b} + (1 - x_{bp}) A_{bj}^k|_{j \neq b} \tag{10b}$$

$$RVI = RVP^{1.25} \tag{11}$$

For bio-blendstocks, the volumetric equivalent RVP was regressed using the results from the Aspen Plus simulation detailed in Section 2.1.1. The volumetric equivalent distillation temperatures (T10, T50, T90) were regressed from the experimentally measured distillation curve [23,25]. The volumetric equivalent octane numbers (Q_i^{ON}) and their binary interaction parameters (A_{ij}^{ON}) were regressed from the experimental results reported by McCormick et al. [22], where octane numbers of the bio-blendstocks and commercial blendstock for oxygenate blending (BOB) at different blending levels were carefully measured using industrial standard methodologies.

2.1.3. Prices, supplies and demands

Table 4 summarizes the prices, supplies, and demands of all blendstocks and products considered in this work. The prices of butane, gasoline, and ethanol were set based on the 5-year nationwide averaged wholesale prices reported by U.S. Energy Information Administration (EIA), Bloomberg, and U.S. Department of Agriculture from 2013 to 2017 [28,34,35]. Note that the price of naphtha streams is not available in open sources; a subscription service may be required [36].

Therefore, the estimated prices at the gate for the petroleum-based blendstocks (c_i) in this blending optimization (Fig. 2) were approximated using the wholesale prices of conventional gasolines ($p_{regular}$) and the incremental value of octane number ($\frac{p_{premium} - p_{regular}}{AKI_{premium} - AKI_{regular}}$) as shown in Eq. (12), a method recommended by S&P Global Platts [21]. The maximum supply of each petroleum-based blendstock was set based on the mass balance given by an example refinery LP model available in Aspen PIMS called Gulf Coast, which represents large-scale and complex petroleum refineries [19]. In this representative refinery, light cracker naphtha and heavy cracker naphtha come from the fluidized catalytic cracking unit; light straight-run naphtha comes from the atmospheric distillation column; isomerate, reformate, and alkylate come from isomerization, catalytic reforming, and alkylation units; and some of the reformate is separated into raffinate and benzene, toluene, and xylene by aromatics extraction.

$$c_i = p_{regular} + (AKI_i - AKI_{regular}) \frac{p_{premium} - p_{regular}}{AKI_{premium} - AKI_{regular}} \tag{12}$$

The volume share of each petroleum-based blendstock listed in Table 4 is within the typical ranges reported by Devenish [36] and Oil Prices Information Service [37,38]. The minimum supply of total petroleum-based blendstocks and minimum demand of total gasoline products were set up such that adding bio-blendstock will not significantly affect the capacity factor or even configurations of major operating units in existing petroleum refineries. The maximum demand of premium gasoline was constrained due to the difference in the current market demands of regular and premium gasoline.

2.2. Break-even value of bio-blendstocks

Spot crude evaluation, which is offered by Assay Management in Aspen PIMS, is widely used in the petroleum industry to rapidly ascertain the break-even value (BEV) of a new crude to a known reference case [39–41]. Refinery planners will then compare this calculated BEV with the delivered price of new crude to determine their crude oil purchasing plan. This work focuses on the potential economic impacts that result from differences in the properties of bio-blendstocks. To answer this question, the analysis boundary is set at the gates of a hypothetical gasoline blender, even though refinery profitability is affected by numerous other factors. Here, BEVs of bio-blendstocks (c_b^{be}) are calculated by Eq. (13) using the same methodology, illustrating the potential economic value of the bio-blendstock to refiners. In Eq. (13), c_b is the cost of bio-blendstock (b) used in the blending optimization model, and E is the value of the objective function defined in Eq. (1) for the blending optimization described in Section 2.1. Superscript (0) represents the known reference case without adding the bio-blendstock, while superscript (n) represents a new scenario blended with the bio-blendstock volume $v_b^{(n)}$ [19]. Because bio-blendstocks are feedstocks for gasoline blending, they can offer economic value to the refineries if their delivered refinery gate prices (the sum of production, transportation, storage, and other logistics costs) are lower than the BEV calculated by Eq. (13). Note that the BEV calculated by this approach is different from the MFSP calculated by techno-economic analysis of biorefinery. As shown in Fig. 4, bio-blendstock is a product from biorefineries, at meanwhile, also a feedstock to the petroleum refineries for gasoline blending. A bio-blendstock's MFSP to a biorefinery reflects the minimum product selling price that allows a biorefinery to achieve a net present value of zero, and it depends heavily on biomass cost and the techno-economics of the conversion technologies. A lower MFSP is preferred for better economics. On the other hand, its BEV to a petroleum refinery is essentially the maximum delivered price of a new bio-blendstock at the refinery

Table 2
Neat properties of petroleum-derived gasoline-range blendstocks [15,33].

	LCN	HCN	LSR	ISM	RFN	RAF	ALK	TXM
Specific gravity	0.682	0.775	0.620	0.650	0.796	0.695	0.695	0.848
RVP (psi)	11.1	1.2	19.7	13.8	7.8	4.9	5.1	0.4
Sulfur (ppm, wt)	2	5	12	10	10	2	2	8
Olefins (vol%)	38	7.8	0.5	0.1	0.6	2.3	1.5	2
Aromatics (vol%)	10	49	0.2	2	70	5	0	83.9
Benzenes (vol%)	0.2	0.16	0.6	0	0.5	0.1	0	0.8
RON	92.3	85.9	75.0	86.0	99.6	67.6	95.0	102.9
MON	81.5	77.7	70.0	83.6	88.0	64.3	92.0	96.9
T10 (°F)	109	235	113	104	144	158	158	280
T50 (°F)	137	288	144	118	250	176	212	282
T90 (°F)	218	376	163	160	316	194	356	282

LCN = hydrotreated light cracker naphtha; HCN = hydrotreated heavy cracker naphtha; LSR = light straight run naphtha; ISM = isomerate; RFN = reformate; RAF = reformer raffinate; ALK = alkylate; TXM = toluene/xylene mixture

Table 3
Neat properties of butanes and bio-blendstocks [23].

	NC4	IC4	ETH	I3L	N3L	I4L	DI4	C5O	FRM
Formula	C_4H_{10}	C_4H_{10}	C_2H_6O	C_3H_8O	C_3H_8O	$C_4H_{10}O$	C_8H_{16}	C_5H_8O	
Specific gravity	0.584	0.563	0.794	0.790	0.810	0.800	0.720	0.940	0.903
RVP(1) (psi)	52.0	71.0	2.3	1.8	0.9	0.5	1.5	0.4	3.5
RON	93.8	98.6	109	109	104	105	106	101	102
MON	89.6	97.6	90	97	89	90	86.5	89.4	87
Oxygen (wt%)	0	0	34.8	26.6	26.6	21.6	0	19.0	18.0
Normal boiling point (°F)	30.2	10.9	173.1	180.5	206.6	226.4	213.8	267.8	
LHV(2) (MJ/kg)			25.54	30.7	30.8	33.2	44.3	33.4	32.2

NC4 = n-butane; IC4 = *iso*-butane; ETH = ethanol; I3L = *iso*-propanol; N3L = *n*-propanol; I4L = *iso*-butanol; DI4 = diisobutylene; C5O = cyclopentanone; FRM = furans mixture (40 wt% 2-methylfuran, 60 wt% 2,5-dimethylfuran)
(1) RVP is approximated by vapor pressure at 100 °F for pure component.
(2) Lower heating value (LHV) of bio-blendstocks were reported by McCormick et al. [23].

gate that would maintain at least the same profitability margins. Therefore, the BEV of the bio-blendstock to the refinery, as defined in this analysis, is closely linked to fuel properties (such as octane numbers and RVP), the finished fuel specifications, and the price of different gasoline blendstocks and products. A higher BEV indicates a more attractive bio-blendstock from the property perspective. For a fair comparison, it is recommended to exclude any government subsidy or renewable tax credit when calculating MFSP and BEV of bio-blendstocks. The difference between the BEV and the delivered price of bio-blendstocks determines the potential economic benefits of blending bio-blendstocks. With a similar delivered price, the higher the BEV, the higher the potential economic value that can be brought to refineries by those blendstocks. This work focused on the BEV evaluations of bio-blendstocks. The location of bio-blendstock blending is irrelevant to this gate-to-gate analysis, while more details about the MFSP evaluations and rankings can be found in the works of Gaspar and Dunn et al. [18,29].

In this work, the BEVs were evaluated at seven scenarios as summarized in Table 5. EIA estimated that in 2018, 142.8 billion gallons of finished motor gasoline were consumed in United States containing about 14.38 billion gallons of fuel ethanol, approximating 10% of the total volume of finished motor gasoline consumption [28]. Since ethanol has already entered the U.S. gasoline pool, with a well-established market, price discovery and regulatory requirements of its use (the federal Renewable Fuel Standard), gasoline blended with 10 vol% ethanol is selected as the base case scenario (0) for comparison. To evaluate the potential value of these bio-blendstock candidates in a future fuel market, it is assumed that the bio-blendstocks listed in

Table 4
Prices, supplies and demands of blendstocks and products.

	Minimum (10^3 BPD)	Maximum (10^3 BPD)	Estimated Prices at the Gate ($/bbl)
Petroleum-based blendstocks			
Light cracker naphtha		22	82.92
Heavy cracker naphtha		15	70.78
Light straight run naphtha		3	48.65
Isomerate		4	77.92
Reformate		25	99.34
Raffinate		11	33.06
Alkylate		12	98.63
Toluene/xylene mixture		8	113.86
Total petroleum-based blendstocks	80	100	
C4′s, ethanol, and bio-blendstocks			
N-butane		10	49.64
I-butane		10	54.02
Ethanol		40	81.86
Bio-blendstocks		40	81.86
Products			
Reformulated regular gasoline			88.62
Reformulated premium gasoline		40	100.80
Total gasoline	100		

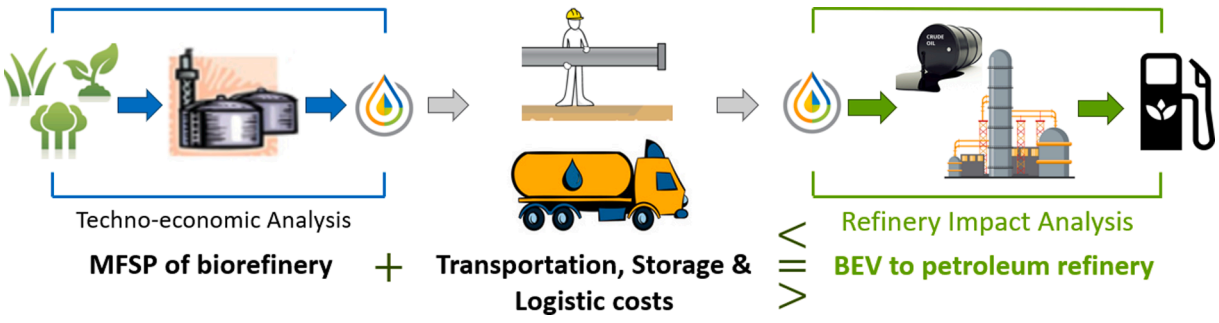


Fig. 4. Break-even value to petroleum refinery vs minimum fuel selling price to biorefinery.

Table 5
Summary of the blending level of ethanol and bio-blendstocks in different scenarios.

Scenario	0*	1	2	3	4	5	6	7
Notation	BC	ExBx	ExB10	ExB20	ExB30	E0B10	E0B20	E0B30
Ethanol (vol%)	10	≤10	≤10	≤10	≤10	0	0	0
Bio-blendstocks (vol%)	0	≤30	10	20	30	10	20	30

* base case

Table 3 can be blended into gasoline with or without ethanol, provided all the regulatory standards for oxygenated gasoline are met according to CFR 40 Parts 79 and 80. These regulations establishes that the lawful use of any of the substances or any combination of these substances requires that they be "Substantially Similar" under Section 211(f)(1) of the Clean Air Act, or be permitted under a waiver granted by the Administrator under the authority of Section 211(f)(4) of the Clean Air Act. In the United States, the amount and type of oxygenated blends are tightly constrained by regulations established in CFR 40 Part 80 and more specifically in Subparts C and D. The additional regulatory platform for the introduction of new additives of blendstocks candidates into commerce will require fulfilling the protocols and regulations established in CFR 40 Part 79. The underlying assumption is that a given bio-blendstock could have a similar path to commercialization as that already followed by ethanol and other renewable fuels. Scenario 5 gives a direct comparison between ethanol and other bio-blendstocks at the same blend level, 10 vol%. Note that the model used $/bbl as the price unit to align with petroleum industry. It can be converted into $/gge (gasoline gallon equivalent) using Eq. (14), which can be used to compare with the MFSPs published previously [18,29].

$$c_b^{be} = c_b + \frac{E^{(n)} - E^{(0)}}{v_b^{(n)}} \tag{13}$$

$$c_b^{be}(\$/gge) = c_b^{be}(\$/gal) \times LHV_{gasoline}/LHV_{bio-blendstocks} \tag{14}$$

3. Results and discussions

In Sections 3.1 and 3.2, non-linear property blending rules were developed for bio-blendstock/gasoline mixtures, as detailed. In Section 3.3, the potential economic values of different bio-blendstocks in summer gasoline blend were evaluated and discussed in details for all case scenarios listed in Table 5. In Sections 3.4 and 3.5, sensitivity studies were conducted to evaluate the effect of AKI, seasonal and geographical variations in volatility specifications, and model uncertainties on the calculated economic value of representative bio-blendstocks. In Section 3.6, the effect of gasoline price on the calculated economic value of all bio-blendstocks was evaluated.

3.1. RVP estimation and model validation

The EOS-based approach developed in our previous studies [4] were used to estimate RVP of the final gasoline/bio-blendstock products. The results were then compared with experimental data measured at 10 vol %, 20 vol%, and 30 vol% blend levels. As shown in Table 6, CPA gives better estimates of RVP than other thermodynamic model evaluated in this work. It is an EOS based on a combination of Soave-Redlich-Kwong with the association term of the Wertheim theory first published in 1996, which has been successfully applied to a variety of mixtures containing oxygenates, water, and hydrocarbons [42,43]. The Aspen RVP, SRKKD, and BK10 models have the highest relative errors since they are designed for hydrocarbon mixtures, or at most hydrocarbon-water mixture, and do not have the capability of handling most of the biomass-derived oxygenates. The capabilities of CPA, NRTL, Wilson, UNIFAC, UNIF-DMD for predicting phase behaviors of several hydrocarbon-oxygenate mixtures have been successfully proven [44]. However, the accuracy of NRTL and Wilson highly depends on the availability of the binary interaction parameters between different compounds, while for UNIFAC and UNIF-DMD it highly depends on the availability of the functional group parameters in the property database. Using the inbuilt property database without additional parameter regressions and property measurements, CPA is the best EOS for estimating RVP.

3.2. Volumetric equivalent properties of bio-blendstocks and binary interactions

As mentioned before, the EOS-based approach is too complicated for blending optimization. In this study, simplified blending rules as described in Section 2.1.2, Eqs. (9) and (10), were used to estimate the finished gasoline blend properties. The volumetric equivalent RVP of each bio-blendstock was regressed using the estimates calculated from the Aspen Plus simulation as described in Section 2.1.1, adjusted by the functional group specific relative error reported in Table 6. The volumetric equivalent distillation temperatures (T10, T50, T90) and octane numbers (MON, RON) as well as the binary interaction terms were regressed using experimental data measured at 10 vol%, 20 vol%, and

Table 6
Relative errors between predicted RVP and measured RVP (%).

	Aspen RVP	SRKKD	BK10	CPA	NRTL	Wilson	UNIFAC	UNIF-DMD
Overall performance								
Maximum relative error	0.0	2.7	0.0	9.3	6.2	0.5	10.5	13.0
Minimum relative error	−42.7	−33.4	−41.2	−11.3	19.3	−22.0	−13.2	−11.1
Average relative error	−29.3	−24.0	−30.2	−1.2	5.9	−9.0	−2.5	0.7
Relative error by functional groups								
CARBOB	9.1	1.6	1.6	4.4	−10.1	−15.0	−9.3	−6.6
CARBOB/10 vol% Ethanol (E10)	−35.0	−31.4	−36.2	−9.1	−10.1	−15.0	−9.3	−6.6
E10/Acetate	−23.9	−21.1	−25.9	5.2	−0.1	−3.3	4.9	7.3
E10/Acetate/Aromatic-ether	−27.7	−22.3	−27.4	4.2	2.1	−2.8	2.6	6.2
E10/Alcohol	−33.3	−25.1	−32.6	−3.3	−7.3	−9.8	−5.7	−2.4
E10/Aromatic-ether	−27.6	−23.6	−30.3	2.9	4.2	−3.7	2.5	5.1
E10/Cyclic Acetal	−28.5	−24.8	−31.0	1.5	−8.0	−11.9	#N/A	#N/A
E10/Ketone	−32.4	−29.7	−34.6	−6.1	−8.1	−10.8	−5.4	−1.9
E10/Lactone	−37.5	−33.4	−39.5	−11.3	−13.6	−17.7	−13.2	−11.1
E10/Unsaturated Alcohol	−30.7	−24.3	−32.7	−2.3	−13.1	−15.9	#N/A	#N/A

#N/A: RVP was not estimated in Aspen Plus because of missing parameters related to functional groups.

Table 7
Parameters in Eqs. (9) to (11) for bio-blendstocks (valid at blend level ≤ 30 vol%).

Bio-blendstocks			ETH(1)	I3L	N3L	I4L	DI4	C5O	FRM
RVP (psi)	Eq. (11)	Q_i^{RVP}	17.45	6.07	3.93	2.16	2.13	0.68	5.08
T10 (°F)	Eq. (9)	Q_i^{T10}	109.3	143.6	151.3	178.0	216.9	244.8	166.4
T50 (°F)	Eq. (9)	Q_i^{T50}	24.4	6.4	23.4	137.3	219.4	227.5	143.7
T90 (°F)	Eq. (9)	Q_i^{T90}	266.4	271.8	260.3	294.8	275.6	243.7	299.6
RON	Eq. (10)	Q_i^{RON}	140.6	121.1	121.5	114.2	118.7	113.7	102.0
		A_{bj}^{RON}							38.3
MON	Eq. (10)	Q_i^{MON}	110.1	98.7	95.3	85.0	96.8	83.7	80.0
		A_{bj}^{MON}		6.3	3.6	13.8		15.6	24.9
AKI	Eq. (10)	Q_i^{AKI}	125.4	109.9	108.4	99.6	107.8	98.7	91.0
		A_{bj}^{AKI}		3.2	1.8	6.9		7.8	31.6

(1) The ethanol volume fraction is about 10% in the current U.S. market [28] and also in this study; hence, only 10 vol% data was used for regressing the ethanol model.
ETH = ethanol; I3L = *iso*-propanol; N3L = *n*-propanol; I4L = *iso*-butanol; DI4 = diisobutylene; C5O = cyclopentanone; FRM = furans mixture.

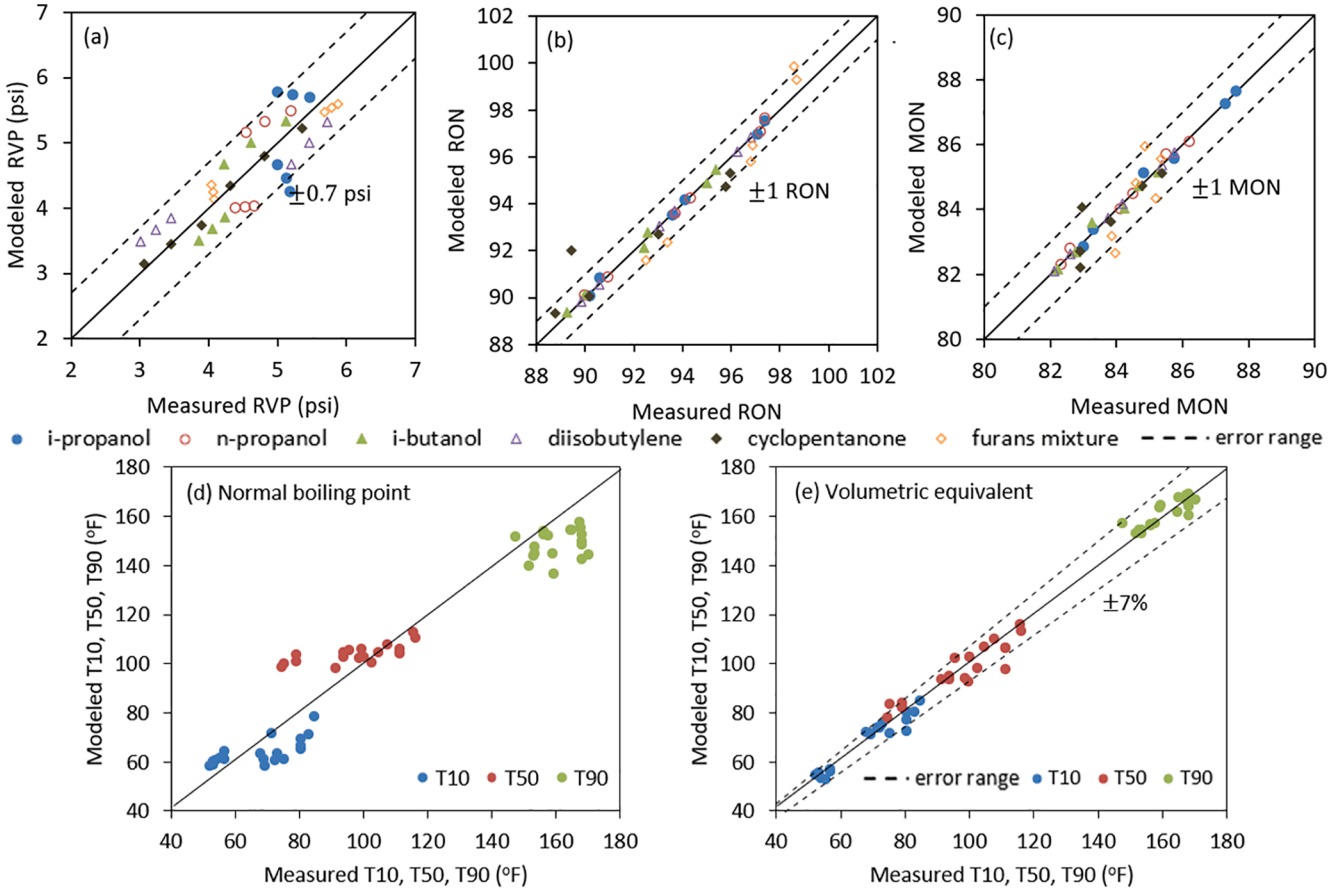


Fig. 5. Validation property blending: (a) RVP, (b) RON, (c) MON, (d) T10, T50, T90 with normal boiling point approach, and (e) T10, T50, T90 with volumetric equivalent approach.

30 vol% blend level and equations described in Section 2.1.2. The regression results are summarized in Table 7. The properties of mixtures predicted by Eqs. (10) and (11) were compared with laboratory-measured data and shown in Figs. 4 and 5. Note that the parameters reported in Table 7 cannot be extended to higher blend levels.

As shown in Fig. 5, the accuracies of the blending models are about ±0.7 psi for RVP, ±1 for RON and MON, and ±7% for T10, T50, and T90. The corresponding uncertainties of economic projections are detailed in Section 3.5. The results indicate these levels of accuracies are acceptable for preliminary screening and value estimation of different bio-blendstocks in the absence of extensive physical property measurements to reduce the uncertainty. To the best of the authors' knowledge, a ± 0.7 psi error in RVP is one of the lowest seen in the open literature for RVP prediction by theoretical methods and built-in correlations and databases in commercial software [4]. In Fig. 5(d), it was assumed that the distillation curves of bio-blendstocks and hydrocarbons could be blended linearly, and therefore T10, T50, and T90 of bio-blendstocks could be approximated by their normal boiling point listed in Table 3. Obviously, Fig. 5(d) indicates that this assumption does not work for bio-blendstock/gasoline mixture. In Fig. 5(e), volumetric equivalent T10, T50, and T90 of bio-blendstocks (Q_i^{T10}, Q_i^{T50}, Q_i^{T90}) listed in Table 7 were used, which match the experimental measurements much better with errors of ±7%. Therefore, in this blending optimization work,

volumetric equivalent T10, T50 and T90 were used. As shown in Table 7, the non-linearity in octane numbers of those bio-blendstocks ranks as furans mixture > cyclopentanone > *iso*-butanol > *iso*-propanol > *n*-propanol. For all bio-blendstocks except diisobutylene, volumetric equivalent T50 is significantly lower than volumetric equivalent T10 and T90, and normal boiling temperature, which suggests a strong non-linear near-azeotropic behavior and matches the experimental observation in distillation curves [23,25]. The non-linearity in volatility, especially T50, ranks as *iso*-propanol > *n*-propanol > *iso*-butanol > furans mixture, cyclopentanone > diisobutylene. By comparing with the pure component properties of bio-blendstocks listed in Table 3, it is observed that the blendstocks with higher vapor pressure will likely have higher volumetric equivalent RVP, and lower T10, even though the values are significantly different from each other.

3.3. Potential economic value of bio-blendstocks in summer gasoline blends (Class AA)

As discussed in Section 2.2, the potential economic value of a new blendstock can be evaluated by the calculated BEV. Since bio-blendstocks are feedstocks to refinery gasoline blending, the higher the calculated BEV, the more additional value a bio-blendstock will potentially bring to a refinery. The delta between the BEV and the delivered price of bio-blendstock is the key driver for the refinery optimal economic scenario. A detailed discussion is provided in this section for the potential value of bio-blendstocks in the summer gasoline blend, while a simple comparison between the summer and winter gasoline blends is provided in Section 3.4. The summer gasoline blend was selected as our analysis focus because it has more stringent fuel specifications, particularly for RVP, while meeting summer gasoline specifications is of much greater significance for these low-RVP bio-blendstocks. The results of all case scenarios listed in Table 5 are

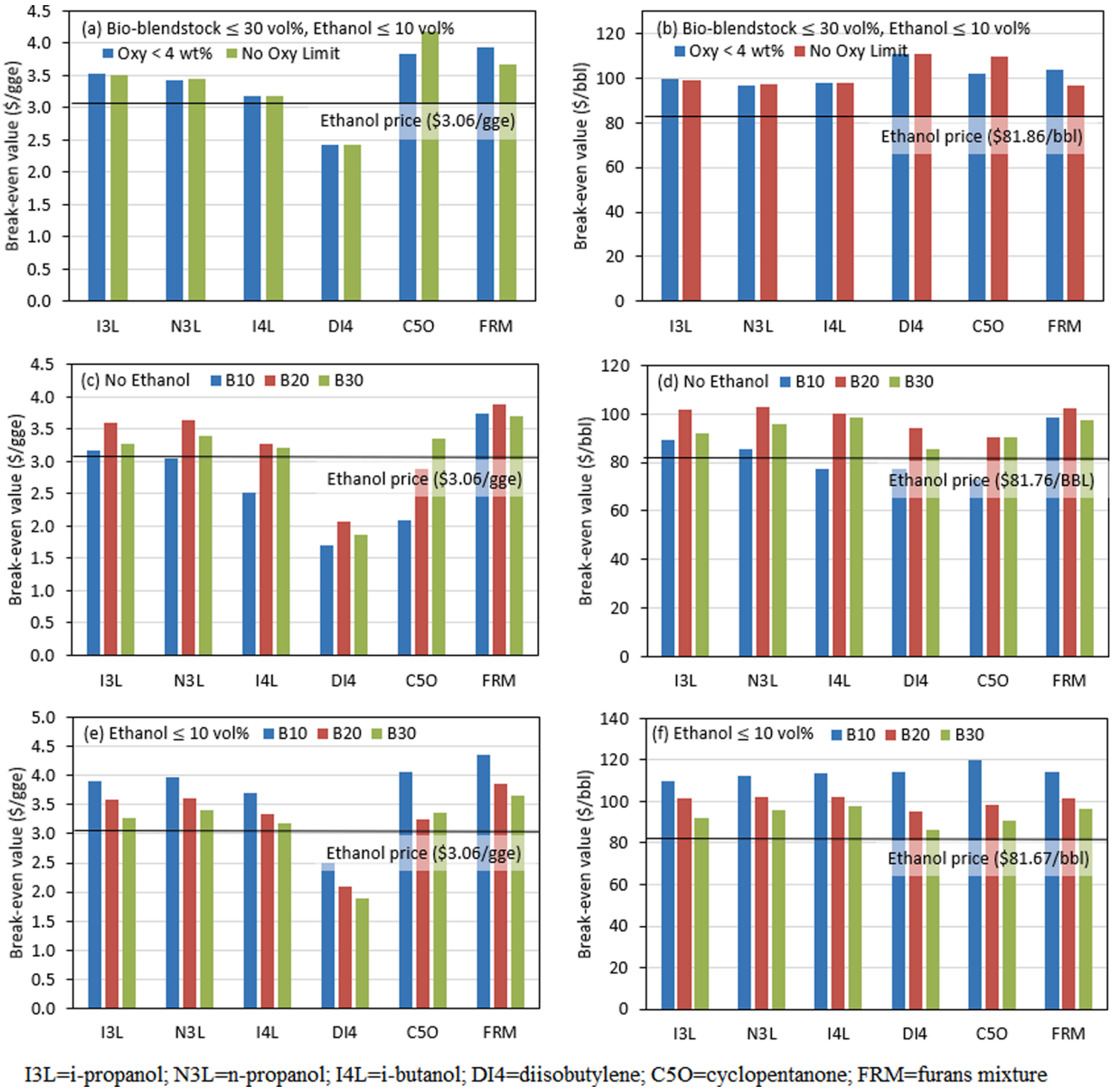


Fig. 6. Potential economic values of bio-blendstocks in summer gasoline blends (a, b) ethanol ≤10 vol%, bio-blendstocks ≤30 vol%; (c, d) ethanol = 0, bio-blendstocks = 10/20/30 vol%; (e, f) ethanol ≤10 vol%, bio-blendstocks = 10/20/30 vol%.

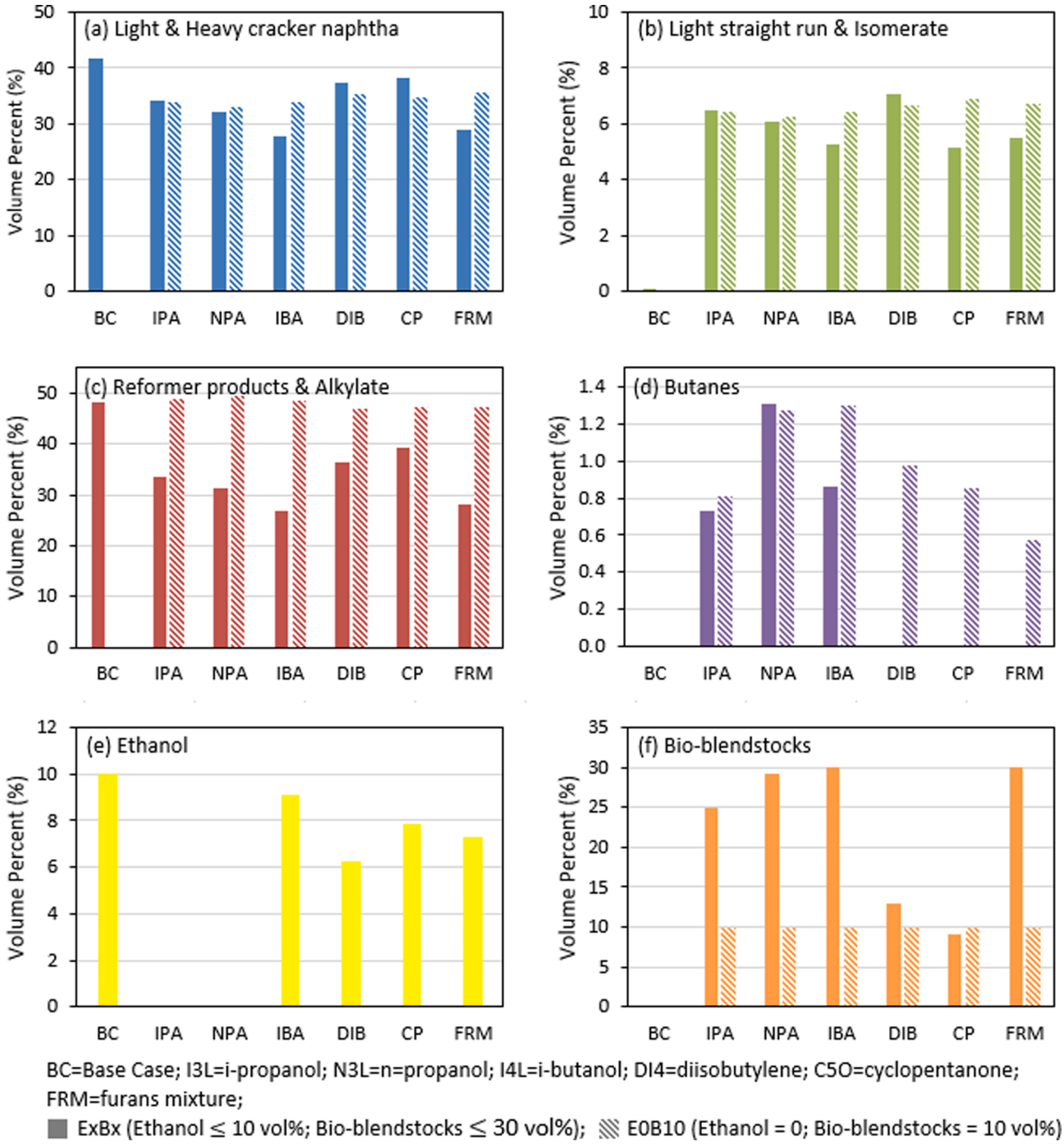


Fig. 7. Volume percent of key blendstocks in summer gasoline blends.

presented in Fig. 6 for a typical summer gasoline blend specified in Table 1. Note that in Fig. 6, BEV is reported in two different units, $/bbl and $/gge. Here, $/bbl is based on the actual volume of the bio-blendstocks, while $/gge is based on the gasoline equivalent volume adjusted by the heating value, as shown in Eq. (14). Fig. 7 provides the volume percent of key blendstocks for the base case (BC), the 10 vol% bio-blendstock scenario (E0B10), and the ethanol $\leq$ 10 vol% scenario (ExBx). For scenario E0B10, the volume percent is marked by bars filled with line pattern. For scenario ExBx and BC, it is marked by solid bar. Table 8 summarizes the properties of finished gasoline that are at the bound of property specifications listed in Table 1. Fig. 8 plots the correlation between bio-blendstock's BEV and its blending properties. The results indicate that the potential economic values of bio-blendstocks are strongly correlated to their properties, blend level, and whether ethanol is present.

As shown in Fig. 6(b), all the bio-blendstocks have a calculated BEV higher than the market price of ethanol in terms of $/bbl when adding them to an E10 blend (ethanol $\leq$ 10 vol%). It indicates that those low-vapor-pressure bio-blendstocks have the potential to bring more value to refineries even if their production costs are higher than ethanol. The calculated BEV of bio-blendstocks can be also reported in terms of $/gge, a unit widely used in the world of biofuels, by converting the value in Fig. 6(b) using Eq. (14). Fig. 6(a) shows that most of the bio-blendstocks have a calculated BEV greater than ethanol in terms of $/gge, except diisobutylene. This is mainly because diisobutylene is a hydrocarbon, which has a much higher heating value than ethanol and is closer to the

Table 8
Variables at upper or lower constraints during blending optimization (BC & ExBx).

	BC	I3L	N3L	I4L	DI4	C5O	FRM
Supplies and Demands							
Total petroleum streams		min	min				min
Reformulated Premium	max	max	max	max	max	max	max
Properties							
RVP (psi)	max	max	max	max	max	max	max
T10 (°F)					max	max	
T50 (°F)		min	min				
AKI	min			min	min	min	
Oxygen (wt%)		max	max	max		max	max

I3L = i-propanol; N3L = n-propanol; I4L = i-butanol; DI4 = diisobutylene; C5O = cyclopentanone; FRM = furans mixture

heating value of gasoline, as shown in Table 3. When adding bio-blendstocks to an E10 environment with the oxygen content limited (scenario ExBx, with ethanol's value of $3.06/gge or $1.94/gal), the calculated BEV in $/gge ranks as furan mixture ($3.9/gge) > cyclopentanone > *n*-propanol ≈ *iso*-propanol > *iso*-butanol > diisobutylene ($2.4/gge). In $/bbl, it ranks as diisobutylene > furan mixture > cyclopentanone > *iso*-propanol > *iso*-butanol > *n*-propanol. The order changes because of the differences in heating values as shown in Eq. (14) and Table 3. Other than diisobutylene, all candidates have a BEV higher than $2.5/gge, the 2030 research goal for biofuel's MFSP set by the U.S. Department of Energy, Bioenergy Technologies Office (BETO). Note that those candidates rank differently in fuel properties, technology readiness, economic viability (from the MFSP perspective) and environmental impacts [18,29]. It will require a comprehensive analysis in all those perspectives to determine the top candidates for gasoline blending. The purpose of this manuscript is to provide a method and basis to compare bio-blendstocks from the perspective of refinery economics and fuel properties.

In addition, Fig. 6(c) to 6(e) indicate that the calculated BEVs of bio-blendstocks also vary with the blending levels and whether ethanol is present. Most of bio-blendstocks have higher calculated BEV when ethanol is present, especially at lower blending levels (e.g., 10 vol%). Without the presence of ethanol, most of the bio-blendstocks have a higher calculated economic value at the 20 vol% blending level.

The calculated BEVs of those bio-blendstocks are different mainly because of the differences in their properties, especially those that were at the upper or lower bound of the gasoline specifications. As shown in Table 8, when adding bio-blendstocks to an E10 blend (ExBx, ethanol ≤ 10 vol%, bio-blendstocks ≤ 30 vol%), the upper limit of oxygen content is reached for all bio-blendstocks except in the base case (of which the constraint on ethanol volume percent is reached first (10 vol% ethanol ≈ 3.7 wt% oxygen)), and the diisobutylene case (since diisobutylene is not an oxygenate). Fig. 6(a) and (b) also presents the results without an oxygen limit. No significant difference is observed since oxygen content only affects the maximum amount of oxygenates that can be blended into gasoline when other constraints are not activated. This does not have a significant impact on the blending volume of petroleum derived blendstocks. In the following cases, the oxygen content limit is removed to allow high oxygenate blend levels.

Table 8 also indicates that RVP, T10, T50, and AKI of the finished products are at the boundaries of gasoline standards. Corresponding to Fig. 7, those properties of bio-blendstocks will significantly affect the blending volume of petroleum blendstocks in the finished gasoline pool and therefore the potential economic values of bio-blendstocks. Fig. 7(d) indicates that, at both low and high levels, all bio-blendstocks allow higher blending fractions of butanes than ethanol does, mainly because they have lower RVP and higher T10 than ethanol.

Moreover, Fig. 6(d) and Fig. 8 indicate that in the E0 blend (the ethanol-free environment), the calculated BEVs of bio-blendstocks are a strong function of their volumetric equivalent blending AKI. According to Fig. 6(d), the calculated BEV at 20 vol% blend level is higher than that at 10 vol% blend level because all bio-blendstocks are acting like octane boosters. However, it decreases at 30 vol% blend level because bio-blendstocks have increasing impact on RVP, T10, T50, and T90 constraints at high blend levels. Fig. 7(c) indicates that at low blend level, for most new bio-blendstocks the blending fractions of high-octane hydrocarbon blendstocks (RON ≥ 95), such as reformate and alkylate, are slightly higher than that of the 10 vol% ethanol case (BC), except for the furan mixture. That is because most of those new bio-blendstocks considered here have lower blending octanes than ethanol. However,

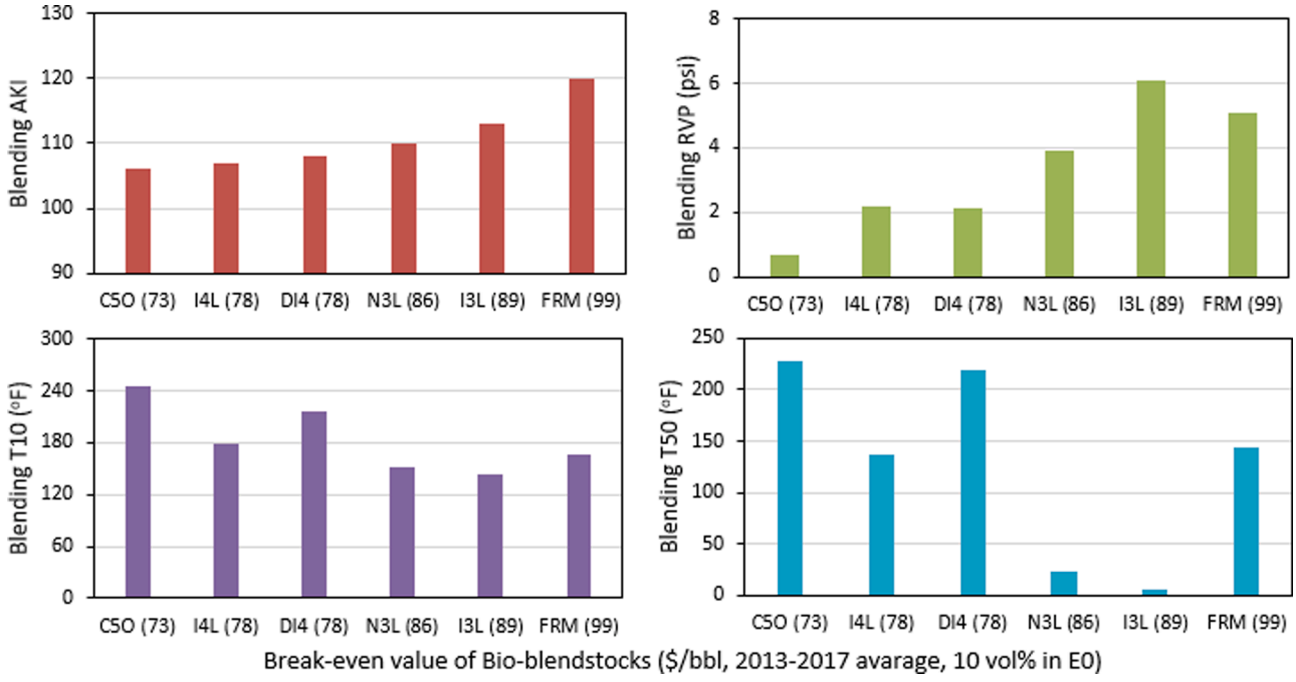


Fig. 8. Potential economic values versus fuel properties in summer gasoline blends (I3L = i-propanol; N3L = n-propanol; I4L = i-butanol; DI4 = diisobutylene; C5O = cyclopentanone; FRM = furans mixture).

Table 9
Directional impacts of blending levels, ethanol blend, and property constrains.

	Calculated BEV	Blending fraction
Higher oxygen upper limits	Decrease for most bio-blendstocks	Increase
Blending with ethanol	Increase for all bio-blendstocks	Decrease
Heavier volatility classes	Increase for E10 blend	Decrease
Higher octane demands	Increase for all bio-blendstocks and scenarios	Increase

as shown in Fig. 7(a) and (b), those bio-blendstocks reduced the call for petroleum blendstocks with mid-level octane ($85 \leq RON \leq 95$), such as light and heavy cracker naphtha and isomerate. At higher blend levels with ethanol, as shown in Fig. 7(c) and (f), those bio-blendstocks can also reduce the call for high-octane blendstocks. In Fig. 8, blending properties are plotted for each bio-blendstock with BEVs in a summer gasoline blend from the lowest to the highest BEVs. A strong correlation is observed between octane numbers and the bio-blendstocks' BEVs. Bio-blendstocks with higher octane number will likely have higher potential economic value to refiners. Correlations between BEVs and volatility properties are not as obvious as those of octane numbers, because RVP, T10, and T50 are interrelated.

As shown in Fig. 6(e) and (f), when blending additional bio-blendstocks into ethanol environment (ethanol $\leq$ 10 vol%), the effect of octane number on the calculated economic values of bio-blendstocks becomes weaker since ethanol is a much stronger octane booster than most of the bio-blendstocks investigated in this work (see Table 7). For the same reason, the potential economic value decreases with the increasing blending level. Fig. 7 indicates that blending both ethanol and new bio-blendstocks into gasoline can significantly reduce the call for expensive high-octane petroleum blendstocks. Therefore, as shown in Fig. 6(a) to (f), most of the bio-blendstocks have higher potential economic value in the 10 vol% ethanol environment than in the ethanol-free environment, especially at low blend levels.

Table 9 summarized the impacts of blending levels, ethanol blending, and property constrains observed and deduced from Figs. 5 to 7 and Table 8. Sensitivity studies were also conducted to analyze the directional impacts of the key property constraints on the calculated BEV of bio-blendstocks. Detailed discussions can be found in Section 3.4.

3.4. Effect of constraints on volatility and high-octane gasoline demands

Table 10 lists the six volatility classes specified by ASTM D4814 in the United States. The selection of volatility classes varies with regions and seasons. In this study, Class AA was selected as the baseline for the summer gasoline blend, and the results were discussed in Section 3.3. In this section, the impact of volatility specifications on the potential economic value of bio-blendstocks was evaluated and presented in Fig. 9 (a) for *iso*-propanol in all volatility classes (AA, A, B, C, D, and E) and in Fig. 9(b) for all bio-blendstocks in the E0B10 bland with representative summer (Class AA) and winter gasoline blend (Class E) specifications.

Fig. 9(a) indicates that the selection of D4814 class (constraints on volatility) has strong impacts on the calculated BEV of bio-blendstocks. When the *iso*-propanol blend level is a variable that can be optimized in an E10 blend (ExBx), the calculated BEV of *iso*-propanol increases with the increasing RVP upper limit, since more cheaper butanes can be blended into gasoline. However, the optimal *iso*-propanol blend level decreases with the decreasing RVP upper limit because the T10 specification becomes harder to satisfy. Consequently, without having ethanol in the system to offer additional flexibility in RVP and T10, the calculated BEV of *iso*-propanol decreases with the RVP upper limit. At 30 vol% blend level (E0B30), it is infeasible to satisfy the T10 specification with Volatility Classes C, D and E. These trends are likely because *iso*-propanol has relatively low RVP but high boiling point. Fig. 9(b) indicates that the other bio-blendstocks investigated in this work have similar trends as those for *iso*-propanol, where BEVs decrease when the RVP upper limit is at a 10 vol% blend level without ethanol. Fig. 9(b) also indicates that all investigated bio-blendstocks have lower BEVs in the winter blend than in the summer blend. This may occur because a low RVP is not required in the winter blend. In addition, a lower T10 is preferred by the winter gasoline but is hard to satisfy with low-RVP blendstocks. Furthermore, without ethanol, it is infeasible to blend>10 vol% bio-blendstock, which has extremely low RVP and high T10 (i.e. diisobutylene, cyclopentanone), into Class E winter gasoline. As shown in Fig. 9(a), to maximize the economic value of low-RVP bio-blendstocks in winter gasoline blend, it is recommended to blend them with ethanol.

Table 10
ASTM D4814 Vapor pressure and distillation temperature classes [12].

Class	RVP (psi)	T10 (°F)	T50 (1) (°F)	T90 (°F)
AA (baseline, summer)	< 7.8	< 158	170–250	< 374
A	< 9.0	< 158	170–250	< 374
B	< 10.0	< 149	170–245	< 374
C	< 11.5	< 140	170–240	< 365
D	<13.5	<131	170–235	< 365
E (winter)	<15.0	<122	170–230	< 365

(1) For gasoline blended with ethanol and bio-blendstocks, T50 minimum is 150°F [12,30].

As shown in Table 6, for all bio-blendstocks the upper limit on the demands of premium fuel were achieved. Since all bio-blendstocks have superior octane ratings than most of the petroleum-derived blendstocks, they may have higher economic value when the demands on high-octane fuel increases. Studies indicated that fuels with higher octane rating ($RON > 100$) and higher octane sensitivity ($S > 8$) may have higher efficiency for spark ignition engines and better fuel economy [29,45]. It is reasonable to assume the gasoline specifications on octane number may change along with research and development activities in motor engines in the future. Though the future gasoline specifications on octane number are not clear at this point, a sensitivity study was conducted by removing the 40 bpd upper limit on premium gasoline to reveal the future opportunities of bio-blendstocks in a high-octane environment to some extent. Here, *iso*-propanol was selected as an example of which the calculated BEV at different blend levels are shown in Fig. 10. The notation of blend levels was defined in Table 5. Similar trends are expected for other bio-blendstock since they all have a superior octane rating.

3.5. Effect of uncertainties from volatility and octane number blending rules

As indicated in Fig. 5, the blending rules implemented in this study will introduce ±0.7 psi errors on RVP, ±1 error on AKI, and ±7% errors on T10, T50, and T90. *Iso*-propanol was selected to represent a bio-blendstock with relatively high volatility and octane numbers. The uncertainties were evaluated at both the optimal blend level (ExBx) and low blend level (E0B10). As shown in Table 11, uncertainties from property blending rules will lead to roughly $0.5/gge (about 15%) uncertainty in the potential economic value of bio-blendstocks.

3.6. Potential effect of market wholesale prices of gasoline

Up until late 2019, a close relationship between ethanol, gasoline,

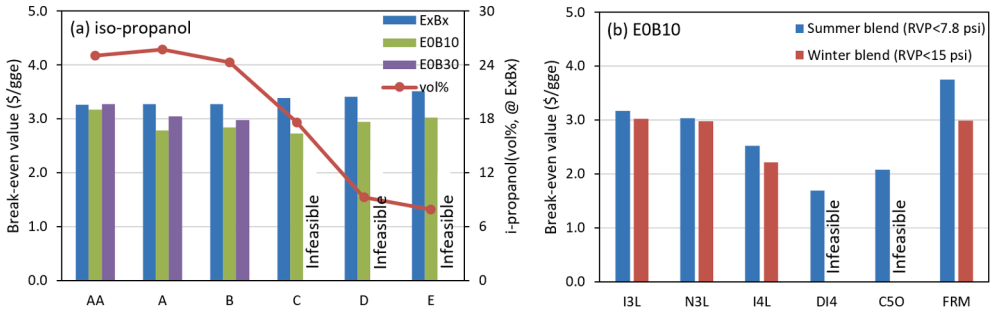


Fig. 9. Impact of volatility classes on the potential economic values of bio-blendstocks: (a) BEV of *iso*-propanol in all volatility classes, (b) BEVs of bio-blendstocks in summer and winter gasoline blends.

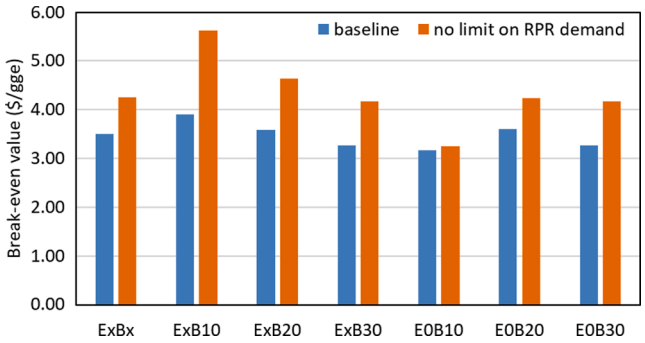


Fig. 10. Potential economic value of *iso*-propanol in summer gasoline blend with high octane demands (blend level notation defined in Table 5).

Table 11
Uncertainties in the potential economic value of bio-blendstocks ($/gge).

	ExBx	E0B10
RVP ± 0.7 psi	−0.08 to 0.09	−0.21 to 0.53
AKI ± 1	0	0 to 0.01
T10 ± 7%	0	−0.10 / 0
T50 ± 7%	−0.07 to 0.10	0
T90 ± 7%	0	0

and crude oil prices was observed in the U.S. fuel market as reported by EIA, USDA and other institutes [28,31,32,46]. In this simplified blending optimization approach, the estimated refinery gate prices of petroleum intermediates were back calculated from wholesale gasoline prices as discussed in Section 2.1.3. To investigate if the potential economic value of bio-blendstocks will follow similar trends or phenomena, a sensitivity study was conducted to evaluate the effects of gasoline prices (which is obviously affected by the crude oil prices). In previous sections, the 2013–2017 5-year average market prices of gasoline, butane, and ethanol were used to evaluate the potential economic value of bio-blendstocks. Here, yearly averages were used to evaluate the effect of gasoline market prices on the potential economic value of bio-blendstocks at 10 vol% blend level. The market prices of wholesale gasoline, ethanol [28,31,32] as well as the calculated BEV of bio-blendstocks are plotted in Fig. 11 from 2013 to 2017 pricing basis. As shown in Fig. 11, the ranks of calculated BEV of bio-blendstocks stay the same when the market price of wholesale gasoline changes from $1.66/gal (2016) to $2.99/gal (2013). The change in calculated BEV of bio-blendstocks follows the change in market prices of gasoline closely. This indicates that bio-blendstocks have the potential to enhance economics of refiners at high gasoline/crude oil price scenarios.

4. Conclusions

In this work, a blending optimization model was developed to evaluate the potential economic value of six low-vapor-pressure bio-blendstock candidates (*iso*-propanol, *n*-propanol, *iso*-butanol, diisobutylene, cyclopentanone, and furans mixture). To the best of authors' knowledge, few studies have been conducted in the open literature to evaluate opportunities for increasing demand for biofuels and bio-blendstocks from the perspective of fuel properties, potential economic value and petroleum refineries. Moreover, an EOS-based model and reduced order non-linear property blending models were developed to have better property estimates. Reid vapor pressure, distillation temperatures, and octane numbers were identified as key property drivers of adding bio-blendstock, of which octane numbers have the most significant effect on the potential economic value of bio-blendstocks. Adding high octane bio-blendstocks can reduce the call

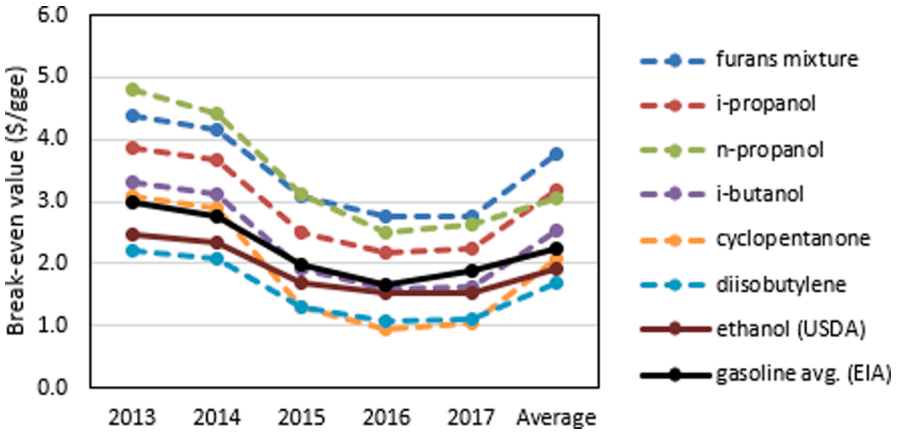


Fig. 11. Effect of gasoline prices on bio-blendstocks' BEV (10 vol% in summer gasoline blend).

for high-octane petroleum-derived blendstocks, which are typically expensive to produce at refineries. In summer gasoline blend, all these low vapor pressure bio-blendstocks allow higher blending fractions of butanes (the cheapest gasoline blendstocks) to be blended in the finished gasoline pool and therefor create economic values. The economic values of low vapor pressure bio-blendstocks in the winter gasoline blend are relatively lower than those in the summer blend, because a low RVP is not demanded in the winter gasoline blend, while the lower T10 specification is hard to satisfy. The calculated BEVs of the bio-blendstocks range from $2.4 to $3.9 U.S. per gasoline gallon equivalent in 2013 to 2017 5-year averaged pricing basis. Except diisobutylene, all bio-blendstock candidates have a BEV higher than the market price of ethanol, as well as BETO's 2030 targets for biofuels' MFSP, $2.5/gge. Blending these bio-blendstocks into gasoline has the potential to bring additional value to petroleum refineries if they can be produced at costs lower than their potential economic values to petroleum refineries by state-of-art technologies or further research and development on production pathways. The sensitivity studies indicate the potential economic value of a bio-blendstock correlates strongly with their properties, blend level, and whether ethanol is present. Uncertainties in property predictions may lead to 15% deviation in the calculation of potential economic value. In addition, the potential economic value of a bio-blendstocks also depends on demands on high-octane gasoline, and the market price of wholesale gasoline. These findings can be used to guide future R&Ds to identify and down-select new bio-blendstock candidates based on their fuel properties.

Note that the approach used here for evaluating the potential economic values of bio-blendstocks is a simplified approach. The S&P Platts' approach for estimating the prices of petroleum-derived blendstocks may lead to some bias in the results. The flowrate of those refinery intermediate streams varies from refinery to refinery because of the difference in crude oil types and plant configurations. The flowrate may also vary when adding new bio-blendstocks, which was not accounted for in this model. For more rigorous estimates of the potential economic value of a bio-blendstock, solving a full refinery LP planning problem (as described in the introduction section) is recommended if process data are available. In a follow up manuscript that is currently in preparation by our group, we have deployed full refinery models built using LP tools to model a complete refinery operation and measure the breakeven value. Finally, to further eliminate the uncertainties in property predictions, more research is required to measure fuel properties and develop blending rules.

CRediT authorship contribution statement

Yuan Jiang: Methodology, Writing - original draft. **Steven D. Phillips:** Methodology, Writing - review & editing. **Avantika Singh:** Writing - review & editing. **Susanne B. Jones:** Writing - review & editing, Supervision. **Daniel J. Gaspar:** Writing - review & editing, Funding acquisition.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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