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The formulation of a base fuel for gasoline-type bioblendstocks

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ABSTRACT

An increasing proportion of biofuels and/or bioblendstocks incorporation in commercial fuels could represent a transition towards the decarbonization of the transportation sector through the proposed electrification strategy. Any biofuel or bioblendstock cannot satisfy all ASTM required specifications. To meet the whole set of specifications, several components (blendstocks) are mixed together. In the case of bioblendstocks, a base fuel composed of oil-derived refinery blendstocks is required (e.g., naphthas from the distillation, fluidized catalytic cracking, isomerization, alkylation, reforming units, etc.). Previous results indicated an interplay among the properties of the bioblendstock and those of the base fuel that need to be consider for formulating such base fuel. Furthermore, the composition of the base fuel could be adjusted to maximize the value-added to bio-refiners, refiners, and blenders. This work confirms the validity of the hypothesized composition of the base fuel, by blending in prenol as an example of bioblendstock and measuring octane, volatility properties, sulfur content, oxidation stability and existing gums. Prenol represents bioblendstocks characterized by low volatility, and a boosting effect on research octane number (RON) and on octane sensitivity (OS). The evaluated properties met measured ASTM D4814 specifications, with the exception of oxidation stability, which could be easily met by using one of the typical correcting additives. The advantages of using a base fuel composition and formulation adapted and adjusted to make the best of a given bioblendstock are discussed.

1. Introduction

The decarbonization of the transportation sector will likely require both electrification [1] and increased incorporation of biofuels [2], among other strategies. For (second generation) biofuels market penetration (and as it will become evident below), their origin and nature would require the addition or mixing of some other components to finalize the fuel. In fact, a finished fuel needs to comply with environmental and performance specifications, as well as market specifications to be commercialized. Regarding gasoline, ASTM D4814 [3] is the standard defined by the U.S. Government to regulate the properties in (unleaded[1]) gasoline sold in U.S. and it is based on 40 CFR 79 and 40 CFR 80. Table 1 shows a selected set of properties included in the U.S. gasoline specifications, as per ASTM D4814 [3].

In order to comply with the required specifications, the finished fuel is produced by mixing together several components (blendstocks), resulting from different refining processes, and selected from their gasoline boiling range. Although in complex-large refineries, up to 15 different blendstocks could be available for producing gasoline, the most commonly used blendstocks are obtained from the direct distillation of crude oil (straight-run naphtha [SRN]) and processes, such as fluidized catalytic cracking (FCC), alkylation (alkylate [ALK]), isomerization (isomerate [ISO]), and reforming (reformate [REF]), as exemplified in Fig. 1 [4]. These blendstocks differ in their composition and octane numbers (research octane number, RON and motor octane number, MON) [5]. Their differentiating compositional characteristics and other

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Abbreviations: AKI, antiknock index; ASTM, American Society of Testing and Materials; BB, bioblendstock; BCOB, Blendstock for Co-Optimized Blending; BOB, Blendstock for Oxygenated Blending; BP, boiling point; BSI, boosted spark ignition; C#, Carbon number; EIA, U.S. Energy Information Administration; EPA, Environmental Protection Agency; FRN, full range naphtha; GC, Gas Chromatography; HC, hydrocarbon; HN, heavy naphtha; IEA, International Energy Agency; LN, light naphtha; MON, Motor Octane Number; ON, octane number; OS, octane sensitivity; RON, Research Octane Number; RVP, Reid vapor pressure; TEL, tetra-ethyl lead; t_r, retention time; S, sulfur; VOC, volatile organic compound.

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[1] The US Environmental Protection Agency (EPA) banned leaded gasoline in U.S. since 1996. EPA regulation (59 FR 7716; 2/16/94) prohibits intentional addition of heavy metals.

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Table 1
Selected gasoline specifications according to ASTM D4814.

Property	Specified value/range
Sulfur, ppm, max	80
Benzene, vol%, max	0.62
RVP @ 37.8 °C (100°F), kPa, max	54–103[a]
T_{10}, °C, max	70
T_{50}, °C, min–max	77–121
T_{90}, °C, max	190
FBP, °C, max	225
Residue, vol%, max	2
Drivability index (DI)	569–597[b]
Oxidation stability (Induction period), minutes, min	240
Existent gum (solvent washed), mg/100 ml, max	5

[a] Regulated by season and region.

[b] $DI = 1.5\ T_{10} + 3.0\ T_{50} + T_{90} + 1.33[\text{vol\% Ethanol}]$, for gasoline containing<10 vol% of ethanol. 40 CFR 80.2 set the limits of DI at the refinery or import facility.

Table 2
Examples of composition ranges of gasoline and octane characteristics of blendstocks.

Gasoline blending component	RON	MON	OS	Composition range (vol %) [5]
FCC-naphtha	88–93	78–86	7–10	30–38
Reformate	98–102	86–88	12–14	29–32
Straight-run naphtha	60–67	57–63	3–4	3–4
Alkylate	90–96	89–94	2–4	10–12
Isomerate	80–91	77–88	3–4	4–5
Butanes	94–98	90–96	2–4	5–6
Ethanol	108–109	93–94	13–14	10
Others	–	–	–	1

features were also included in Fig. 1. The differentiating hydrocarbon (HC) family is the family present in the highest concentration for that particular blendstock, compared to what it is for the others. Regarding sulfur (S) content, it is highest for the SRN and the FCC-naphtha and almost negligible for the other blendstocks, for which desulfurization pretreatments have been performed on intermediate streams used for their production.

The octane characteristics for these blendstocks, including RON, MON, and octane sensitivity (OS = RON - MON) are collected in Table 2. Typical blending ranges (in vol%) for each of them, in 10 %- ethanol containing gasoline, [5] are also included in this table. However, the availability of these blendstocks for blending and finishing the gasoline fuel depends on the processed crude slate, the refinery configuration, and the product distribution. Additionally, some of the specified properties have regional and seasonal regulations as well (e.g., RVP), to which the refiner or blender must comply with. Therefore, the HC composition of a given gasoline will vary among regions and seasons and will molecularly depend on the composition of the crude slate from which it originated.

In the case of gasoline, the U.S. Department of Energy's (DOE) Co-Optimization of Fuels & Engines Program (Co-Optima) [6] investigated numerous bioblendstocks (BBs) and advanced engines, such as boosted sparkling ignition (BSI), multi-mode (MM) and advanced compression ignition (*ACI*), and found that fuels exhibit high RON and OS boost efficiency and performance while minimizing emissions. For the present work, these Co-Optima selected BBs (or biofuels) are refer as Co-Optimized BBs.

Most of the international market grades gasoline in terms of RON, while the U.S. market uses the antiknock index (AKI = [RON + MON]/2) for grading the gasoline commercialized in its territory. Currently, three grades are being marketed in the U.S., regular (AKI = 87), mid-range (AKI = 89), and premium (AKI = 91–93). Thus, improving octane numbers and removing sulfur are mandatory operations to meet both ASTM D4814 (Table 1) and market specifications (e.g., AKI-based grades).

The current renewable component used in the U.S. market is bioethanol, mostly first-generation bioethanol at a typical concentration of 10 vol%. Although the U.S. Environmental Protection Agency (EPA) EPA has already approved the use 15 vol% ethanol in the marketed gasoline, 98 % of the gasoline sold in the USA contains 10 vol% ethanol [7]. U.S. commercial gasoline is composed by a base fuel, produced at

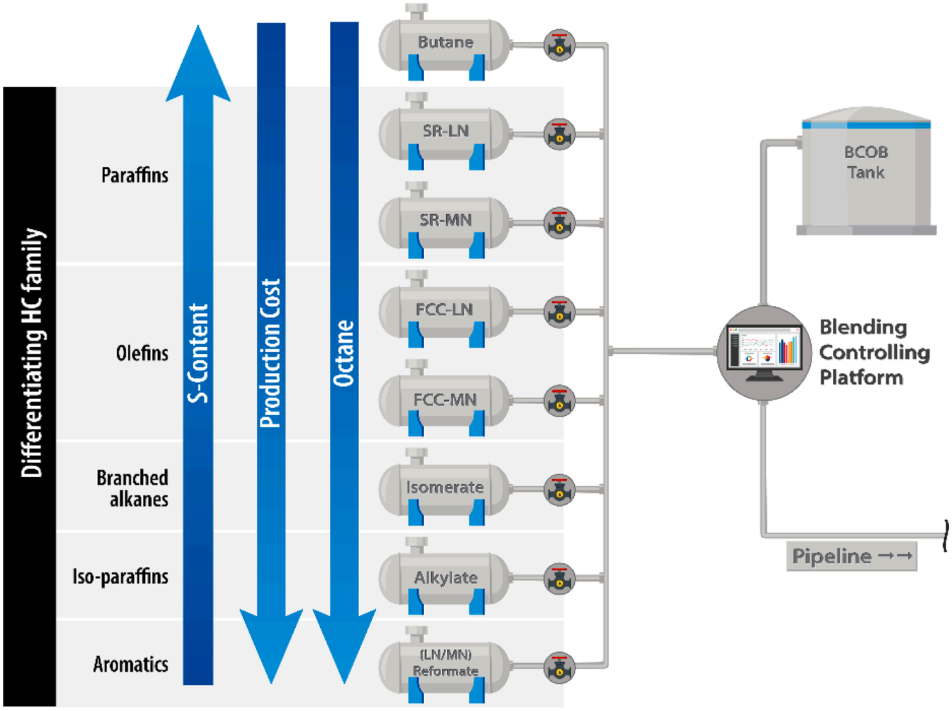

Fig. 1. Refinery blending system and general characteristics and differentiating features of gasoline components ("Adapted from Ref. [4], with permission from Elsevier").

refinery level, and bioethanol that is added prior to distribution to the selling stations. This base fuel is known as "blendstock for oxygenate blending" (BOB). Thus, the current BOB formulations only meet gasoline ASTM D4814 specifications upon addition of about 10 % of bioethanol. Our studies indicate that regardless of the composition, type, or origin of these current BOBs, they are not necessarily suitable for blending any other oxygenated BB or at any other concentration level (blending grade) [4].

Co-Optima has selected 3-methyl-2-buten-1-ol (prenol) as one of the top ten potential candidates for gasoline-type BBs, which maximizes efficiency gain with market potential [8]. Prenol is a C5 olefinic alcohol characterized by its low volatility, or lower vapor pressure(e.g., RVP and high boiling point [BP]), and high boosting power of RON (neat RON of 93.5 and blending RON of 122 – 145) and OS [9].

In a previous work [4], properties exhibiting synergistic behavior were determined by considering binary mixtures of prenol blended volumetrically at 10, 20, and 30 vol%, into each of the full range naphtha (FRN) of the five main gasoline components, namely SRN, FCC, ISO, ALK, and REF. The identified synergistic properties were RON and OS, RVP, and distillation curve–driveability index (DI), and S-content. The observed results indicated there is intrinsic value of a given BB, arising from the combination of a S-dilution effect, with the octane boosting and the low volatility properties. However, non-trivial interplay between the BB properties and those of the fossil component constituted the main evidence for a redefinition of the base fuel composition. Facts such as (i) SRN and FCC are the main contributors to S-content, (ii) around 60 % of the S-compounds are present in the heavy naphtha fraction [10] of these blendstocks, and (iii) typically, BBs do not contain sulfur can be combined to meet the S-content specification of ASTM D4814. Thus, a hypothetical composition of a base fuel for blending prenol-type BBs was proposed, in which the heavy naphtha fraction of the SRN and the FCC-naphtha are not incorporated. In the case of co-optimized BBs with low volatility and high boosting effect of RON and OS (e.g., prenol), the base fuel (blendstock for co-optimized blending, BCOB) formulation might contain less olefins (from FCC light and mid-range naphthas, LN & MRN), less aromatics (from light reformate), and compensate the DI by a balance of the lighter fractions (e.g., light ends and isomerate) [4]. The proposal for lowering the concentration of olefins and aromatics was based on the observation of antagonistic octane blending between prenol and these HC families. Antagonistic octane blending is not new and has been observed with ethanol, for which toluene (as aromatic example) acted against its synergism with isooctane and *n*-heptane (as isoand paraffins examples, respectively) [11]. The tentative range of BCOB composition in terms of component blendstocks is shown in Table 3. This set of parameters was estimated based on the identified properties and exhibited behavior and can be considered a preliminary parametric definition of a BCOB for blending prenol into fossil gasoline components, at blending grades as high as 30 %. The contribution to octane ratings was estimated based on a linear blending assumption and the measured RON and MON of the blendstocks, as reported in Ref. [4].

Table 3
Proposed tentative composition of a finished gasoline, in terms of blendstock components, for meeting S-content specification of 10 ppm [4].

Gasoline Blending Component	Composition vol%	Octane Contribution RON	MON	OS
FCC-Naphtha (LN & MRN)	25–35	29–41	25–35	4–6
Reformate	10–18	12–22	10–18	2–4
Straight-Run Naphtha (LN & MRN)	4–7	4–7	3–6	0–1
Alkylate	15–24	19–30	16–26	2–4
Isomerate	4–6	4–7	4–6	0–1
Butanes	5–6	6–7	7	0
Prenol	20			
Others	1			
Blend		**92–95**	**80–82**	**12–13**

This work examines and analyzes the properties of multi-component blends containing prenol with the purpose of identifying properties exhibiting antagonistic behavior, providing more insights on the properties interplay, and validating the proposed composition of a suitable base fuel.

2. Experimental methods

Binary mixtures of prenol in each of the five main components of gasoline (SRN, FCC, ISO, ALK, REF) were prepared containing 10, 20, and 30 vol% of prenol. These binary blends were considered for the identification of properties showing antagonistic behavior between prenol and the regarding base fuel blendstock. Additional blends were prepared to respond to the proposed BCOB composition, in terms of both fossil blendstocks (BCOB1 and BCOB2) and hydrocarbon families (BCOB3 through BCOB7). The design basis and resulting nominal composition of these blends are detailed in Section 3.2. Chevron, USA, provided the refinery blendstock samples. Analyses of the considered blends were carried out at Intertek Inc. commercial fuel testing facilities in Deer Park, TX. The following analyses were carried out: RON (ASTM D2699), MON (ASTM D2700), detailed hydrocarbon analysis (DHA), ASTM D6730 PIONA (paraffins, isoparaffins, olefins, naphthenes, and aromatics), sulfur content (ASTM D5453), solvent-washed gum content (ASTM D381), and oxidation stability (ASTM D525).

The additional blends used to investigate the effects of different hydrocarbon families were developed by modeling the PIONA from mixtures of blendstocks derived from refinery streams and comparing the results to the hydrocarbon distributions in Table 6. Naphtha, olefinic, and aromatic blendstocks, which had previously been characterized by PIONA, were employed. Blendstocks with carbon numbers from C4 to C13 were used. All blending was performed under laboratory conditions. Once a model was approved, a prototype was developed, tested, and compared to the distributions in Table 6. Any deviations were noted and, if needed, another prototype was created. Finally, larger volumes of the blends were made and considered for this work. Analyses, including RON, MON, DHA, Sulfur, and Gums, were conducted at Gage Products for the hydrocarbon blends (BCOB3 through BCOB7), prior to adding prenol, which was added at 10 and 20 vol%. Those properties were also evaluated for the prenol containing hydrocarbon blends, at Intertek Inc. commercial fuel testing facilities in Deer Park, TX, as indicated above.

3. Results and discussion

Any comparative analysis between the properties of a given BB and bioethanol constitutes evidence indicating that current BOB base fuels cannot be necessarily suitable for blending such BB, and not within a broad range of blending levels. In general, the base fuel formulation would need to be adapted to blend in other BBs different than ethanol. The properties of individual blendstocks affected by a specific BB will differ from one BB to another and these effects can be either positive or negative. The impact of prenol's properties on gasoline blendstocks was taken as the basis to formulate and define a hypothetical composition of a BCOB, which could blend in prenol to finalize a fuel, taking advantage of synergistic blending while meeting ASTM D4814. Using prenol as a low volatility and octane (RON & OS) booster BB could serve as an example for other BBs with similar characteristics. Therefore, the proposed BCOB might also be suitable for those BBs which fall within this spectrum.

3.1. Antagonistic behavior

As mentioned above, prenol was found to synergize well with gasoline blendstocks for improving RON, OS, Reid vapor pressure (RVP), BP, volatile organic compounds (VOCs), and sulfur (S) content [4]. Unfortunately, some other prenol properties antagonize with those of the blendstock and may preclude the finished fuel from meeting some of the ASTM D4814 specifications. In Table 4, the results on the oxidation stability and the existing gums, for binary mixtures of prenol-blendstock showed the negative effect of prenol on these properties.

As can be seen in Table 4, except for the FCC-naphtha, all the blendstocks could pass the oxidation stability specification of an induction period at 100 °C > 240 min. However, upon the smallest addition of prenol (10 %), there was an observed decrease in the induction period below about 60 min, which deviates the blend from meeting this specification for all blends containing prenol. Similarly, the specification of washed gums (<5mg/100 ml) was also met by all the blendstocks, and prenol deteriorated it, precluding attainment for all except the alkylate blends and the reformate containing 10 % prenol. Therefore, we could identify-two properties exhibiting antagonistic behavior, namely oxidation stability and existing gums.

The DHA results of the previously studied binary blends provided indirect evidence that there might exist interactions, at the molecular level among prenol, olefin, and/or aromatic compounds [4]. Since the antagonistic behaviors are aggravated in blendstocks containing larger amounts of olefins and aromatics (Table 4), these interactions might also be responsible, or at least associated with, the observed antagonistic behaviors. Factually then, the compositional framework of a BCOB for prenol should minimize the content of olefins and aromatics. Although, a systematic study of the effect of prenol on these HC families, leading to the deterioration of certain properties falls out the scope of the present work, previous results supporting these interactions [4] moved us to carry out spectroscopic characterization of particular blends. The original interest of this spectroscopic characterization was to provide data for modeling purposes. Preliminary results have brought up some insights into the understanding of these phenomena. In particular, DHA and FT-IR results showed specific features that were not exhibited by neither prenol nor the fossil blendstocks. We have been modeling our DHA results and considering surface analysis boundaries obtained when trying to maximize RON, MON, and OS, while introducing specifications as constraints. DHA results of blends of prenol in a base fuel (composed by one or more fossil blendstocks) showed a decrease in the detected amount of prenol and the disappearance of signals present in the base fuel. Meanwhile, the FT-IR results showed multiple indications of the chemical interactions. In addition to the expected variation in the intensity of different spectral features indicating the decrease and increase of certain compounds involved in chemical reactions, there were some new spectral features that were not present in either of the components of the blend. The two most relevant features were new signals appearing in the regions around 1157 cm^{-1} and 1731 cm^{-1}. The former peak might be associated to tertiary alcohols and the latter to aliphatic ethers. These types of compounds have been reported to cause a positive influence in octane numbers [12] and to be chemically related to prenol [13]. However, both the description of the modeling strategy and a more in-depth analysis of potential interactions between those individual compounds falls outside the scope of this work and will be the subject of a future publication.

Table 4
Oxidation Stability and Existing Gums of refinery blendstocks and binary blends with prenol.

Sample	Oxidation Stability	Gums, mg/100 ml	
	Induction period @ 100 °C, min	Washed	Unwashed
SRN	>240	<0.5	3
SRN PR30	16	103.5	105
FCC	221	0.5	5
FCC PR10	62	10.5	12
FCC PR20	31	56.5	60
ALK	>240	<0.5	<0.5
ALK PR10	48	<0.5	<0.5
ALK PR20	43	1.5	3
ALK PR30	31	3.5	9
REF	>240	1	2
REF PR10	54	3	5
REF PR20	37	13.5	14
REF PR30	43	23	24.5
ASTM D4814	>240	<5	–

3.2. Blends design

As mentioned above, two types of base fuels were prepared to respond to the proposed BCOB composition, one set based on refinery blendstocks and the other on hydrocarbon families. The extremes of the tentative composition proposed for the BCOB (Table 3) were the design basis of the first two base fuels (BCOB1 and BCOB2) composed of refinery blendstocks and are shown in Table 5. However, volume limitations of some of the refinery blendstocks did not allow for sufficient preparation of base fuel, for mixing all the desired prenol blending grades. Another point is that these two blends were prepared using the available FRN samples rather than the light and mid-range fractions (suggested in the proposed formulation) since Idaho National Laboratory (INL) does not have gasoline distillation capabilities.

The DHA composition data of the blendstocks was used to calculate the composition of BCOB1 and BCOB2, in terms of hydrocarbon families. This estimated composition was the basis for designing two additional blends: BCOB3 and BCOB4 (Table 6). Finally, three blends were designed for a better understanding of the interplay between hydrocarbons and BBs. For instance, BCOB5 and BCOB6 maximize and minimize, respectively, the aromatics content while BCOB7 eliminates the presence of olefins (Table 6). Furthermore, the employed hydrocarbons were selected to exclude those typically present in heavy naphtha. Although these blends contain a limited number of hydrocarbons (far from comparable to the real blendstocks), insights on the effect of eliminating the heavy fraction and on the individual interplay of compounds could be discovered.

3.3. Fuels and blends assessment

The results for the properties measured on BCOB1, BCOB2, and prenol containing blend samples are collected in Table 7. As can be seen, there were slight differences between the linearly estimated octane values, particularly RON, for the proposed BCOBs (Table 3) and the measured ones (Table 7). These overestimations of RON also led to an overestimation of OS of the proposed BCOB. Remarkably, results (Table 7) significantly exceed the expectations that were derived from those linearly estimated values (Table 3). The extraordinary improvement of RON, with a negligible effect on MON, led to a duplication of OS upon the addition of 20 % of prenol. Regarding S-content, all samples contain < 80 ppm and meet Table 1 specification. However, under the EPA Tier 3 fuel program, S-content specification for gasoline and gasoline-oxygenate blends was set to < 10 ppm on an annual average basis beginning January 1, 2017. The 80 mg/kg and 95 mg/kg are the current per-gallon caps at refinery gate and downstream, respectively. As was mentioned above, the definition of BCOB composition was based on the hypothesis that S-content could be improved by removing the heavy naphtha fractions from the SRN and FCC naphthas and the diluting effect of a S-free BB. However, INL's is not equipped with

Table 5
Composition of blends based on refinery blendstocks.

Gasoline blending component	Composition, vol%	
	BCOB1	BCOB2
FCC-naphtha (light & mid-range)	44	32
Reformate	19	13
Straight-run naphtha (light & mid-range)	5	9
Alkylate	19	30
Isomerate	13	16
Total	100	100

Table 6
Composition of blends based on.hydrocarbon families.

	n-Paraffins	Isoparaffins	Olefins	Naphthenes	Aromatics
BCOB3	11.2	52.0	6.0	7.3	21.2
BCOB4	13.3	48.7	9.0	8.2	18.6
BCOB5	12.5	20.4	6.0	8.0	51.9
BCOB6	12.8	47.4	19.9	8.0	9.6
BCOB7	13.2	55.1	0.0	9.2	19.2
Proposed envelope	**11–17**	**44–55**	**6–9**	**6–9**	**17–22**

standard fuels distillation equipment, so BCOB1 and BCOB2 were prepared using the available full range naphthas rather than the proposed light and mid-range naphthas. Therefore, we are inclined to believed that removal of those fractions will contribute to place the S-specification in the 10 ppm range.

The improvement in gums formation was also remarkable. Regardless of the prenol blending grade, all the considered finished gasoline samples (prenol containing blends) meet the washed gums specification. Finally, although the oxidation stability was not improved to meet the specification, it was not deteriorated as badly as was previously observed for the binary blend samples (Table 4).

The real composition of the blends based on fossil blendstocks (described in Table 5) and on hydrocarbon families (described in Table 6) was measured by DHA ASTM D6730, and the summary results are shown in Fig. 2 (A) and (B), respectively. The high proportion of FCC naphthas in BCOB1 and BCOB2 explains the high concentration of unidentified compounds (Fig. 2 (A)) and makes the comparison somehow cloudy. DHA is known to show discrepancies on the olefins determination due to some interfering co-elution above C7, particularly with samples containing higher boiling cuts derived from FCC (heavy FCC-naphtha) [14]. In terms of the designed formulation, it was expected that the hydrocarbons composition of BCOB3 and BCOB4 simulated those of BCOB1 and BCOB2, respectively. While this seems to have been closely achieved, the olefins discrepancies (of the method) and the high unknowns presence in BCOB1 and BCOB2 introduce uncertainty. Comparing the values of the nominally designed composition of the base fuels (reported in Table 6) with those actually measured composition (as reported in Fig. 2 (B)) indicates that the base fuels fall with very good agreement into the designed principles. As mentioned in Section 3.2, BCOB3 and BCOB4 were defined to fall within the envelope composition of the proposed BCOB, described in Table 3 and summarized in the last row of Table 6. The other three blends, BCOB5, BCOB6, and BCOB7, also agree well with the designed composition. Initially, the composition of the blends containing prenol shows the expected diluting effect of the BB, i.e., decreasing in nearly 10 % or 20 % the original concentration of the base fuel, depending on the prenol blending level. The expected molecular interactions between prenol and some hydrocarbon compounds might lead to higher reductions in olefins and/or aromatics.

The volatility properties of these blends were measured using ASTM D5191 and D86 for RVP and distillation curve, respectively. Table 8 collects the results of these properties and includes the calculated driveability index and the specified values reported in Table 1 to facilitate a comparison and discussion. All blends showed a T_{10} higher than the maximum allowed value because the lightest compounds present are C_5. The lowest T_{10} was observed for BCOB6, which was designed to fit

Table 8
Volatility properties of blends based on hydrocarbon families.

	RVP, psi	T_{10}, °F	T_{50}, °F	T_{90}, °F	DI, °F	DI, °C
BCOB3	3.7	177.8	227.5	301.9	1251	597
BCOB4	3.9	174.7	226.7	300.3	1242	592
BCOB5	2.5	194.5	246.6	295.4	1327	639
BCOB6	4.1	169.3	219.4	289.2	1201	570
BCOB7	3.8	178.6	239.2	328.4	1314	632
D4814 Specs	7.8 – 15.0	158 max	170 min – 250 max	374 max	1200 – 1250	569 – 597

Table 7
Properties results for BCOB1, BCOB2 and prenol containing finished fuel.

Sample	Prenol, vol%	RON	MON	OS	AKI	Oxidation Stab, min	Gums, %		S-Content, ppm
							Unwashed	Washed	
BCOB1	0	87.2	80.9	6.3	84.05	>240	3	<0.5	39
BCOB1 PR10	10	91	80.8	10.2	85.9	101	9	–	33
BCOB1 PR20	20	93.7	80.3	13.4	87	54	8.5	<0.5	26
BCOB2	0	85.1	80	5.1	82.55	>240	2	<0.5	53
BCOB2 PR20	20	92.7	81.2	11.5	86.95	62	11	1	42

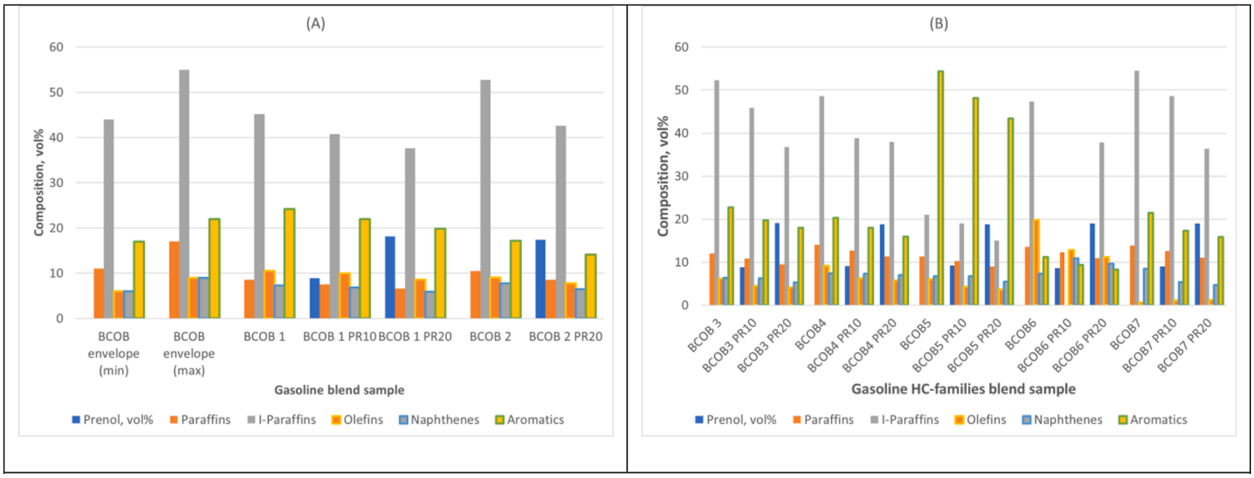

Fig. 2. Composition of blends: (A) based on fossil blendstocks and (B) blends based on hydrocarbon families.

the highest olefinicity. In general, T_{10} inversely correlates with RVP, i.e., the higher the T_{10}, the lower the RVP would be. The required adjustments on both T_{10} and RVP can be done by light-ends (e.g., butanes) addition, in which case a low value stream would shift to a higher value product, as was discussed in a previous work [4]. These high values of T_{10} push the DI towards the top end, but it can be expected that controlling T_{10} will move it towards moderate values. Nevertheless, T_{10} was not high enough to place the DI out of specification for BCOB3 and BCOB4 (within the proposed base fuel formulation). Therefore, the distillation profile/DI specification and the RVP are two (+three boiling temperatures) additional properties that could easily be met by the BCOB formulation.

The measured octane numbers, and derived properties OS and AKI are collected in Table 9, together with the results for oxidation stability, gums, and sulfur content. In these samples, the levels of sulfur are almost undetectable, and the gums are extremely low or inexistent. Regarding octane, the linearly estimated values included in Table 3 were typically higher than these obtained for the hydrocarbon families blends due to the lack of heavier hydrocarbons in these latter blends (it is well established that octane numbers increase with carbon number [5]). The octane characteristics of the different hydrocarbon families, shown in Table 10, are incorporated here for validating and supporting the current observations [5]. One could infer that these reported octane ranges correspond to the octane ratings of the lightest and heaviest family compound potentially present in gasolines. As can be seen in Table 9, all blends exhibited low octane number values, with the exception of BCOB5. Once again, the improving effect of prenol is significant for RON and almost negligible for MON, which directly translates into AKI and OS values. Prior to the prenol addition, none of the hydrocarbon blends could meet the minimum AKI requirements for U.S. Regular grade. OS was also very low for all blends, except for BCOB5. The highest RON and OS in these hydrocarbon families blends were observed for the BCOB5 blend and could be due to a large presence of aromatics and, in a lesser degree, isoparaffins (Fig. 2 (B)). The addition of prenol significantly improves the targeted octane properties (RON and OS) and in a lesser extent, the AKI. The addition of 10v% prenol improved AKI to that of Regular gasoline value for BCOB5; the BCOB3 almost reached the value. Meanwhile, 20 % was more than enough to upgrade to regular grade the BCOB3, BCOB5 and BCOB7 blends. The boosting effect of prenol in the BCOB5, BCOB6, and BCOB7 provides more insights on the relative and mutual effects of olefins and aromatics. Olefins content was (by design) minimized, maximized, or eliminated from BCOB5, BCOB6, and BCOB7 blends, respectively (see Table 6 for design principles and Fig. 2 (B) for resulting composition). Additionally, heavier aromatics and olefins are not present in these blends. It is evident that minimizing olefins (within the proposed envelop formulation, Table 6) leads to a better boosting effect (on both, RON, and OS) than eliminating the olefins.

Table 10
Octane properties of hydrocarbon families [5].

	RON	MON	OS
n-Paraffins	<19 Very low	<19 Very low	0 Very Low
Isoparaffins	90–100 High	86–100 High	<3 Low
Naphthenes	80–85 Low	70–80 Low	>3 Medium
Aromatics	**>100 Very High**	**>95 High**	> 12 High
Olefins	90–95 High	70–80 Low	**>15 Very high**

While oxidation stability is not as deteriorated by prenol as the refinery blends (BCOB1 and BCOB2) were, the gums pass ASTM D4814 specification, excepting BCOB5 PR20. Whether this observation is the result of the hypothesized interactions between prenol and aromatics or an experimental error or outliner value will need to be confirmed in a later work.

In summary, the present work has demonstrated the validity of the BCOB proposed formulation, for blending in a BB, such as prenol, and to provide benefits to refiners and bio-refiners while meeting finished gasoline specifications. Fig. 3 exemplifies the suggested blending process for BCOB production in oil refineries to enable refiners to take advantage of the intrinsic value that BBs can add to their products, by eliminating some (SRN and FCC) heavy naphtha fractions from the base fuel composition.

4. Conclusions

This work describes the advantages of using a base fuel composition and formulation adapted and adjusted to make the best of a given bioblendstock. The tentative composition of BCOB proposed was based on the observed interplay of BB properties and on the base fuel components in binary mixtures and was defined to meet S-specification considering a contribution of 60 %-S from the heavy fraction of SRN and FCC naphthas. Meanwhile, this work validated these hypotheses and confirmed that at least two specified properties (washed gums and S-content) can be met by a finished fuel, containing 10 to 20 % BB. Furthermore, the results also indicate that more than these two specified properties could be met at these blending grades as well as at higher blending grades. Thus, the working space envelope for formulating BCOBs has been validated by formulating a BCOB within the established framework and verifying that more than two properties of the corresponding blend containing the bioblendstock fall within the ranges specified in ASTM D4814.

Declaration of Competing Interest

The authors declare that they have no known competing financial

Table 9
Octane, oxidation stability, gums, and S-content of blends based on hydrocarbon families.

	RON	MON	OS	AKI	Oxidation Stability, min	Gums, mg/100 ml		S-Content, ppm
						Unwashed	Washed	
BCOB3	83.9	82.1	1.8	83	>240	2.2	1.4	1.2
BCOB3 PR10	89.2	82.4	6.8	85.8	63	3	1	
BCOB3 PR20	93.1	82.4	10.7	87.75	44	4	3.5	
BCOB4	80.4	76.9	3.5	78.65	>240	0	0	1.1
BCOB4 PR10	86.4	78	8.4	82.2	121	3	<0.5	
BCOB4 PR20	90.7	81.3	9.4	86	61	3	1.5	
BCOB5	91.1	81.3	9.8	86.2	>240	1	0	0
BCOB5 PR10	94.1	81.3	12.8	87.7	168	3	0.5	
BCOB5 PR20	94.7	80.8	13.9	87.75	42	12	11.5	
BCOB6	75	72.1	2.9	73.55	>240	0	0	1.1
BCOB6 PR10	81.4	73.2	8.2	77.3	61	3	1	
BCOB6 PR20	86.4	77.8	8.6	82.1	36	5.5	3.5	
BCOB7	80	77.4	2.6	78.7	>240	2	0	0.9
BCOB7 PR10	86.9	78.5	8.4	82.7	92	3.5	<0.5	
BCOB7 PR20	91.5	83	8.5	87.25	52	3.5	<0.5	

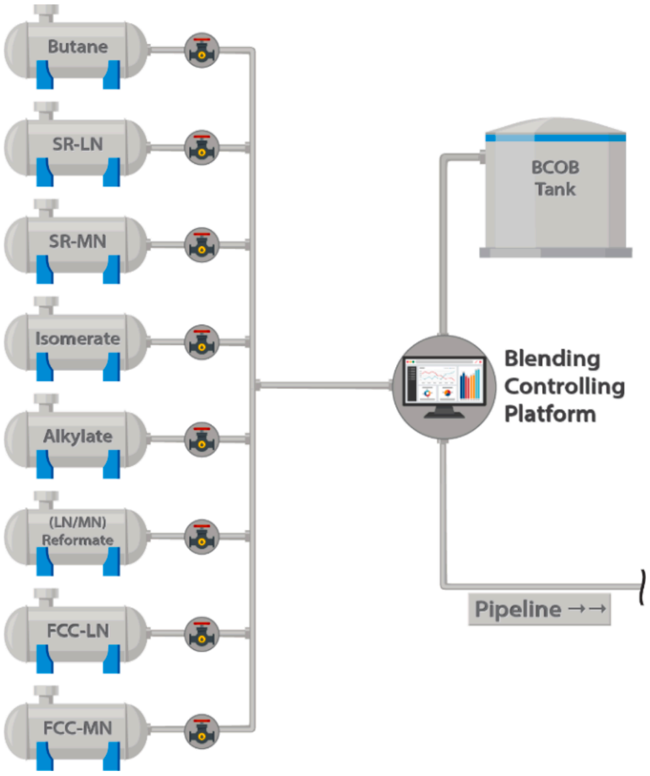

Fig. 3. BCOB production.

interests or personal relationships that could have appeared to influence the work reported in this paper.

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