REDUCED RVP OXYGENATED GASOLINE COMPOSITION AND METHOD

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 Related U.S. Application Data

 Continuation-in-part of application No. 12/902,251, filed on Oct. 12, 2010, which is a continuation of application No. 11/332,997, filed on Jan. 17, 2006, now abandoned. Continuation-in-part of application No. 12/364,905, filed on Feb. 3, 2009.

 Provisional application No. 60/646,741, filed on Jan. 25, 2005, provisional application No. 61/027,969, filed on Feb. 12, 2008.

 ABSTRACT

 Compositions of oxygenated gasolines are disclosed that have reduced vapor pressure compared to those containing a single oxygenate and no RVP reducing compound. Such compositions can be formed at a refinery or at a terminal. Methods of reducing vapor pressure of an oxygenated gasoline are disclosed and methods of reducing vapor pressure constraints upon a refinery in the production of oxygenated gasoline are disclosed. Fundamental properties of RVP reducing compounds are disclosed including IR spectrum analysis. Processes and methods for blending and distributing these fuels are also disclosed.
FIGURE 1

Relative Absorbance

Oxygenate Compound, wt%
Figure 3

Ethanol, volume % in Unleaded Regular Gasoline

RVP, psi

0  2  4  6  8  10  12

7.6  7.4  7.2  7  6.8  6.6  6.4  6.2  6
REDUCED RVP OXYGENATED GASOLINE COMPOSITION AND METHOD

CROSS-REFERENCE


BACKGROUND OF THE INVENTION

[0002] This invention relates to fuels, more particularly to oxygenated gasoline including gasoline containing ethanol. This invention provides an oxygenated gasoline having a reduced Reid vapor pressure (RVP) thereby allowing a higher proportion of low boiling components to be blended into the gasoline without exceeding RVP limits. This invention also provides a method for reducing the RVP of oxygenated gasoline.

[0003] Gasolines are fuels which are suitable for use in a spark-ignition engine and which generally contain as a primary component a mixture of numerous hydrocarbons having different boiling points and typically boiling at a temperature in the range of from about 26° C. to about 225° C. under atmospheric pressure. This range is approximate and can vary depending upon the actual mixture of hydrocarbon molecules present, the additives or other compounds present (if any), and the environmental conditions. Typically, the hydrocarbon component of gasolines contain C4 to C10 hydrocarbons.

[0004] Gasolines are typically required to meet certain physical and performance standards. Some characteristics may be implemented for proper operation of engines or other fuel combustion apparatuses. However, many physical and performance characteristics are set by national or regional regulations for other reasons such as environmental management. Examples of physical characteristics include RVP, sulfur content, oxygen content, aromatic hydrocarbon content, benzene content, olefin content, temperature at which 90 percent of the fuel is distilled (T-90), temperature at which 50 percent of the fuel is distilled (T-50) and others. Performance characteristics can include octane rating (also called anti-knock index), combustion properties, and emission components.

[0005] For example, standards for gasolines for sale within the United States are generally set forth in ASTM Standard Specification Number D 4814-01a (“ASTM 4814”) which is incorporated by reference herein. Additional federal and state regulations supplement this standard.

[0006] The specifications for gasolines set forth in ASTM 4814 vary based on a number of parameters affecting volatility and combustion such as weather, season, geographic location and altitude. For this reason, gasolines produced in accordance with ASTM 4814 are broken into volatility categories AA, A, B, C, D and E; and vapor lock protection categories 1, 2, 3, 4, 5, and 6, each category having a set of specifications describing gasolines meeting the requirements of the respective classes. This specification also sets forth test methods for determining the parameters in the specification.

[0007] For example, a Class AA-2 gasoline blended for use during the summer driving season in relatively warm climates must have a maximum vapor pressure of 54 kPa, a maximum temperature for distillation of 10% volume of its components (the “T10”) of 70° degree C., a temperature range for distillation of 50% volume of its components (the “T50”) of between 77° C. and 121° C., a maximum temperature for distillation of 90% volume of its components (the “T90”) of 190° C., a distillation end point of 190° C., a distillation residue maximum of 2% volume, a “Driveability Index” or “DI” maximum temperature of 59° C., where DI is calculated as 1.5 times the T10 plus 3.0 times the T50 plus the T90 and a maximum vapor to liquid ratio of 20 at a test temperature of 56° C.

[0008] One physical characteristic of gasolines that is addressed in ASTM 4814 and is commonly regulated in many jurisdictions is RVP. RVP can be measured in accordance with ASTM Standard Specification D 5191-04a (“D 5191”) which is incorporated by reference herein. RVP standards are typically expressed as a maximum RVP limit which gasolines sold commercially in a particular jurisdiction may be compelled to meet. Such RVP limits significantly constrain the composition of hydrocarbons in gasolines because RVP increases as the proportion of lighter hydrocarbons increases. Typically, to produce gasolines with reduced RVP, the proportion of lighter hydrocarbons, for example C4 hydrocarbons, are reduced. Decreasing such lighter hydrocarbons can negatively impact gasoline characteristics. For example, decreasing the amount of butane in a gasoline fuel lowers the RVP of that fuel, but it also reduces the octane rating.

[0009] By constraining the composition of gasolines, RVP limits also impose a burden upon refineries. Generally, refineries adjust the composition of gasolines by controlling the proportions of various refinery streams which are used to produce the gasolines. For example, to produce a gasoline with a higher boiling point, a refinery may need to reduce the proportion of low-boiling refinery streams used to produce the gasoline. To produce gasolines which will satisfy applicable RVP limits, refineries typically reduce the proportion of lighter boiling hydrocarbons in gasolines. RVP is typically controlled or adjusted using empirically determined RVP blending values. A RVP blend value represents a particular composition’s contribution to the RVP of a particular mixture. One consequence of such RVP constraints upon refineries is that less gasoline can be refined from each barrel of petroleum. This can significantly impact the gasoline supply available to meet consumer demand.

[0010] The impact of RVP limits has intensified because of the increasing use of oxygenates in gasolines. Oxygenates are used in gasolines to increase the chemical oxygen content. Unfortunately, oxygenates have a non-linear effect upon RVP when blended into a fuel. Therefore, RVP blending values of oxygenates are determined empirically for a particular concentration of a particular oxygenate in a particular fuel. Many jurisdictions have oxygenate requirements for gasolines to promote more complete combustion.
ether (MTBE) was a commonly used as a gasoline oxygenate. However, many jurisdictions prohibit or severely limit the use of MTBE and similar ethers.

Because of the restrictions on use of MTBE, ether oxygenates with less favorable RVP are typically used in gasoline. Ethanol is widely used as an oxygenate because of a number of factors including tax credits offered by many jurisdictions for use of up to 10 vol % ethanol in gasoline. U.S. Pat. No. 6,258,987 to Schmidt et al. and U.S. Pat. No. 6,540,797 to Scott et al., which are incorporated by reference herein, discuss blending ethanol in gasoline. Unfortunately, many of the oxygenates permitted for blending into gasoline have significant drawbacks including an affinity for water which causes transportation and handling difficulties, and an increase in a gasoline’s RVP when blended with the oxygenate. An affinity for water causes transport and handling difficulties. RVP increase amplifies the difficulty of producing gasoline within applicable RVP limits. Ethanol exhibits both of the foregoing effects.

There is a need for a composition or method to lessen the detrimental effects which can result from blending oxygenates into gasoline. In particular, it would be desirable to counter at least some of the RVP increase attributable to blending oxygenates into gasoline.

We have found that certain compounds can exhibit unexpectedly low RVP blending values for blending with typical oxygenated gasolines. Surprisingly, in some cases, such compounds can even exhibit negative RVP blending values.

This invention lessens the RVP increase attributable to oxygenate blending into gasoline which allows refineries to use a higher proportion of low-boiling hydrocarbons in gasoline blend stocks thereby increasing the gasoline refining capacity of the refinery. This invention can be used to reduce the RVP of an oxygenated gasoline. In certain instances where an oxygenated gasoline is blended which has an RVP value exceeding the applicable maximum RVP limit, this invention can be used to make the oxygenated gasoline comply with the RVP limit.

SUMMARY OF THE INVENTION

We have found that use of a RVP reducing compounds, as further described herein, can have a surprising RVP reducing effect upon oxygenated gasolines. Such RVP reducing compounds can interact with an oxygenate to lower the RVP increase expected from blending the oxygenate with a gasoline blend stock. In some cases, the RVP reducing compound’s effect is so dramatic that the RVP reducing compound exhibits a negative RVP blending value.

This invention provides an oxygenated gasoline which can meet an applicable RVP limit and can still include a greater amount of lighter components than would otherwise be possible. This invention allows a refinery to use a greater proportion of crude for gasoline thereby increasing the supply of gasoline. This invention also provides a method of reducing the RVP of an oxygenated gasoline. Such reduction can be performed at a terminal and can help reduce the necessity of obtaining waivers for gasoline which may otherwise have an RVP exceeding regulations. This invention also provides a method of reducing the RVP constraint upon gasoline blend stocks for oxygenate blending in the production of oxygenated gasolines for jurisdictions having a maximum RVP limit.

In one embodiment, we provide a gasoline containing a gasoline blend stock, a suitable oxygenate, and an effective amount of a RVP reducing compound. Preferably, the RVP reducing compound has a RVP blend value less than about 3.0 psi, more preferably less than about 0.0 psi. Optionally, the RVP value of a mixture of the gasoline blend stock and the suitable oxygenate is at least about 6.9 psi. Preferably, the suitable oxygenate is an alcohol, more preferably ethanol. The RVP reducing compound can be selected from a group consisting of 2-propanol, 1-butanol, 2-butanol, tert-butanol, 1,3-propanediol, 2,3-butanediol, acetic acid and combinations thereof. Preferably greater than 2 vol % suitable oxygenates are present. Preferably, less than 15 vol % RVP reducing compounds are present. More than one suitable oxygenate can be used. More than one RVP reducing compound can be used.

In another embodiment, a method of reducing the RVP of an oxygenated gasoline is provided. The method includes a step of blending a gasoline blend stock and one or more suitable oxygenates to form an oxygenated gasoline, and the step of mixing the oxygenated gasoline and one or more RVP reducing compounds wherein at least one RVP reducing compound has a RVP blend value less than about 3.0 psi, preferably less than about 0.0 psi. The suitable oxygenate can be an alcohol, preferably ethanol, and the RVP reducing compound can be selected from the group consisting of 2-propanol, 1-butanol, 2-butanol, tert-butanol, 1,3-propanediol, 2,3-butanediol, acetic acid and combinations thereof. Either or both of the blending or mixing steps can be performed at a terminal. Optionally, the blending step can be performed contemporaneously with the mixing step. Preferably greater than 2 vol % suitable oxygenates are present. Preferably, less than 15 vol % RVP reducing compounds are present.

In another embodiment, a method of reducing the RVP constraint upon a gasoline blend stock in the production of oxygenated gasolines with a predetermined maximum RVP limit is provided. The method includes the step of blending a gasoline blend stock and one or more suitable oxygenates to form an oxygenated gasoline having a RVP value greater than the predetermined maximum RVP limit, and the step of adding an effective amount of one or more RVP reducing compounds to form a gasoline having a RVP value less than or equal to the predetermined maximum RVP limit. The blending step and the adding step can be performed contemporaneously. The suitable oxygenate is preferably ethanol. The RVP reducing compound can be selected from the group consisting of 2-propanol, 1-butanol, 2-butanol, tert-butanol, 1,3-propanediol, 2,3-butanediol, acetic acid and combinations thereof. Preferably greater than 2 vol % suitable oxygenates are present. Preferably, less than 15 vol % RVP reducing compounds are present.

Relative absorbance, as described further herein, is a useful way to identify particularly effective RVP reducing compounds. Relative absorbance can also be used to identify oxygenated gasolines which are particularly amenable to RVP reduction using an RVP reducing compound. In any embodiment, a gasoline blend stock, one or more suitable oxygenates and one or more RVP reducing compounds can be selected such that a mixture of the gasoline blend stock, suitable oxygenate(s) and RVP compound(s) has a normalized relative absorbance less than about 0.045. Preferably, a blend of the gasoline blend stock and suitable oxygenate(s) has a normalized relative absorbance greater than about 0.05.
BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a graph plotting the relative absorbance of an oxygenated gasoline having two different oxygenates as a function of wt%. Fig. 2 is a bar graph of the relative absorbance of an oxygenated gasoline with several RVP reducing compounds. Fig. 3 is a graph plotting the RVP of an unleaded regular gasoline having a base RVP of 6.1 psi as a function of the volume percent of ethanol in that gasoline.

DESCRIPTION OF THE PREFERRED EMBODIMENT(S)

Gasolines are well known in the art and generally contain as a primary component a mixture of hydrocarbons having different boiling points and typically boiling at a temperature in the range of from about 26°C to about 225°C. Under atmospheric pressure, this range is approximate and can vary depending upon the actual mixture of hydrocarbon molecules present, the additives or other compounds present (if any), and the environmental conditions. Oxygenated gasolines are a blend of a gasoline blend stock and one or more oxygenates.

Gasoline blend stocks can be produced from a single component, such as the product from a refinery alkylation unit or other refinery streams. However, gasoline blend stocks are—more commonly blended using more than one component. Gasoline blend stocks are blended to meet desired physical and performance characteristics and to meet regulatory requirements and may involve a few components, for example three or four, or may involve many components, for example twelve or more.

Gasolines and gasoline blend stocks optionally may include other chemicals or additives. For example, additives or other chemicals can be added to adjust properties of a gasoline to meet regulatory requirements, add or enhance desirable properties, reduce undesirable detrimental effects, adjust performance characteristics, or otherwise modify the characteristics of the gasoline. Examples of such chemicals or additives include detergents, antioxidants, stability enhancers, demulsifiers, corrosion inhibitors, metal deactivators, and others. More than one additive or chemical can be used.

Useful additives and chemicals are described in U.S. Pat. No. 5,782,937 to Colucci et al. which is incorporated by reference herein. Such additives and chemicals are also described in U.S. Pat. No. 6,083,228 to Wolf and U.S. Pat. No. 5,755,833 to Ishida et al. both of which are incorporated by reference herein. Gasolines and gasoline blend stocks may also contain solvent or carrier solutions which are often used to deliver additives into a fuel. Examples of such solvents or carrier solutions include, but are not limited to, mineral oil, alcohols, carboxylic acids, synthetic oils, and numerous other which are known in the art.

Gasoline blend stocks suitable for the composition of this invention are typically blend stocks useable for making gasolines for consumption in spark ignition engines or in other engines which combust gasoline. Suitable gasoline blend stocks include blend stocks for gasolines meeting ASTM 4814 and blend stocks for reformulated gasoline. Suitable gasoline blend stocks also include blend stocks having low sulfur content which may be desired to meet regional requirements, for example having less than about 150 ppmw sulfur, more preferably less than about 100 ppmw sulfur, more preferably less than about 80 ppmw sulfur. Such suitable gasoline blend stocks also include blend stocks having low aromatics content which may be desirable to meet regulatory requirements, for example having less than about 8000 ppmv benzene, more preferably less than about 7000 ppmv benzene, or as further example, having less than about 35 vol % total aromatics content, more preferably less than about 25 vol % total aromatics content. As used herein “total aromatics content” refers to the total amount of all aromatic species present.

“Oxygenate” as used herein means a C3 to C6 compound containing only carbon, hydrogen and one or more oxygen atoms. For example, oxygenates can be alcohols, ketones, esters, aldehydes, carboxylic acids, ethers, ether alcohols, ketone alcohols and poly alcohols. Ethanol is a preferred oxygenate for several reasons including its widespread availability. “Suitable oxygenate” as used herein means an oxygenate which has a RVP blend value of at least 6.5 psi and which is soluble in the particular oxygenated gasoline being produced. Preferably greater than about 2 vol % oxygenate is present.

“RVP blend value” or “blend RVP” is the effective RVP of a composition when blended into a fuel mixture. A blend RVP value represents the contribution of the blend component to the RVP of a mixture such that the RVP for the mixture equals the summation of each component’s RVP value multiplied by that component’s volume fraction. For example, for a fuel mixture of [A] and [B], the RVP = (blend RVP of [A] * volume fraction of [A]) + (blend RVP of [B] * volume fraction of [B]).

As used herein, a compound is soluble in a second compound if a mixture of the compounds exhibits a single liquid phase in the desired concentrations over the temperature range of interest which, unless stated otherwise, is from about 40°C to the initial boiling point of the mixture.

“RVP reducing compound” as used herein means a C3 to C6 compound including only carbon and hydrogen and one or more heteroatom each of which is selected from the group consisting of oxygen and nitrogen, which compound is soluble in the selected oxygenated gasoline and which reduces the RVP of the selected oxygenated gasoline when blended into the selected oxygenated gasoline. An effective amount of a RVP reducing compound is an amount which reduces the RVP of the oxygenated gasoline by at least 0.05 psi for the particular RVP reducing compound concentration. RVP can be determined in accordance with ASTM D 5191 using sufficient measurements for a statistically significant determination. Preferably, the total concentration of RVP reducing compound is less than about 15 vol %, more preferably less than about 10 vol %, most preferably no greater than about 5 vol %.

RVP reducing compounds can be alcohols, ketones, esters, carboxylic acids, ethers, ether alcohols, ketone alcohols, poly alcohols, amines, amine alcohols and combinations thereof. Examples of RVP reducing compounds include 2-propanol, 1-butanol, 2-butanol, tert-butanol, 2-butanone, 3-methyl-2-butanone, 4-methyl-2-pentanone, ethyl acetate, butyl acetate, acetic acid, diisopropyl ether, methyl tert-butyl ether, 2-ethoxy ethanol, 4-methyl-4-hydroxy-2-pentanone, 1,3-propanediol, 2,3-butanediol, 2-ethyl hexanol, triethyl amine and combinations thereof.

RVP reducing compounds which are especially effective for reducing the RVP of oxygenated gasolines can be identified by determining the normalized relative absorbance of a mixture of the oxygenated gasoline and the RVP reducing compound. Additionally, suitable oxygenates which are particularly amenable to such specially effective RVP
reduction can be identified by determining the normalized relative absorbance of the oxygenated gasoline (without the RVP reducing compound).

[0033] Without being limited to any particular theory, it is believed that RVP reducing compounds interact with oxygenates in an oxygenated gasoline and increase the tendency of the oxygenate to remain in a liquid phase thereby reducing the RVP of the oxygenated gasoline. Relative absorbance is an analytical technique that can be used to identify suitable oxygenates and RVP reducing compounds which are particularly amenable to such interactions which produce a synergistic reduction of RVP.


[0035] Relative absorbance of a mixture containing a RVP reducing compound and an oxygenated gasoline is determined using the difference spectrum obtained by subtracting the absorbance spectrum of the oxygenated gasoline without any suitable oxygenate from the absorbance spectrum of the mixture and using the two-point baseline method to calculate the ratio of the band area from 3680 cm⁻¹ to 3550 cm⁻¹, to the band area from 3680 cm⁻¹ to 3100 cm⁻¹. Use of the difference spectrum as described minimizes variability due to use of different gasoline blend stocks.

[0036] Relative absorbance of an oxygenated gasoline is determined using the difference spectrum obtained by subtracting the absorbance spectrum of the oxygenated gasoline without the suitable oxygenate from the absorbance spectrum of the oxygenated gasoline and using the two-point baseline method to calculate the ratio of the band area from 3680 cm⁻¹ to 3550 cm⁻¹, to the band area from 3680 cm⁻¹ to 3100 cm⁻¹.

[0037] Table I below shows the relative absorbance of several oxygenated gasolines having differing concentrations of two oxygenate compounds in a fungible unleaded regular gasoline meeting ASTM D 4814. FIG. 1 shows a plot of this data.

**TABLE I**

<table>
<thead>
<tr>
<th>Oxygenate</th>
<th>Concentration wt %</th>
<th>Relative Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethanol</td>
<td>1.05</td>
<td>0.104</td>
</tr>
<tr>
<td>ethanol</td>
<td>2.11</td>
<td>0.049</td>
</tr>
<tr>
<td>ethanol</td>
<td>5.27</td>
<td>0.009</td>
</tr>
<tr>
<td>2-butanol</td>
<td>0.938</td>
<td>0.211</td>
</tr>
<tr>
<td>2-butanol</td>
<td>1.88</td>
<td>0.174</td>
</tr>
<tr>
<td>2-butanol</td>
<td>4.69</td>
<td>0.047</td>
</tr>
</tbody>
</table>

[0038] As shown in Table I and FIG. 1, relative absorbance varies by compound and by concentrations. Table I also demonstrates the non-linearity between relative absorbance and concentration. Relative absorbance will generally be determined empirically. For the particular unleaded regular gasoline used in Table I, both ethanol and 2-butanol would be oxygenate compounds for this particular embodiment of the invention.

[0039] Table II shows the relative absorbance of several mixtures of RVP reducing compounds and an oxygenated gasoline with the same fungible unleaded regular gasoline used for Table I. FIG. 2 is a graph of the data. TABLE-U.S. Pat. No. 00002 TABLE II Relative Absorbance of RVP

**TABLE II**

<table>
<thead>
<tr>
<th>RVP Reducing Compound</th>
<th>Concentration wt %</th>
<th>Relative Absorbance</th>
</tr>
</thead>
<tbody>
<tr>
<td>none</td>
<td></td>
<td>0.049</td>
</tr>
<tr>
<td>2-butanol</td>
<td>2.0</td>
<td>0.015</td>
</tr>
<tr>
<td>methyl ethyl ketone</td>
<td>2.0</td>
<td>0.027</td>
</tr>
<tr>
<td>butyl acetate</td>
<td>3.0</td>
<td>0.037</td>
</tr>
<tr>
<td>triethyl amine</td>
<td>3.0</td>
<td>0.054</td>
</tr>
</tbody>
</table>

[0040] As illustrated in Table I and FIG. 2, adding the RVP reducing compounds into the oxygenated gasoline has a significant impact on the relative absorbance of the mixture. The impact varies with different RVP reducing compounds, but such change in relative absorbance indicates a synergistic interaction between the components resulting in a surprising RVP reducing effect.

[0041] In some embodiments, a RVP reducing compound is selected such that the normalized relative absorbance of a mixture containing one or more RVP reducing compound and an oxygenated gasoline is less than about 0.045, preferably less than about 0.030. Preferably, one or more suitable oxygenates are selected such that the normalized relative absorbance of an oxygenated gasoline containing such suitable oxygenate(s), (without the RVP reducing compound) is greater than about 0.05, preferably greater than about 0.1.

[0042] Normalized relative absorbance of a mixture containing a RVP reducing compound and an oxygenated gasoline is defined as the relative absorbance of the mixture when the RVP reducing compound is present at more than about 0.5 wt % in the mixture at the desired concentration of suitable oxygenate.

[0043] Normalized relative absorbance of an oxygenated gasoline (without a RVP reducing compound) is determined by calculating relative absorbance when the suitable oxygenate is present at about 1.0 wt % in an oxygenated gasoline.

[0044] Preferably, the RVP reducing compound is 2-propanol, 1-butanol, 2-butanol, tert-butanol, 1,3-propanediol, 2,3-butanediol, or acetic acid. More preferably, the suitable RVP reducing compound is 1-butanol, 2-butanol, or tert-butanol. Other examples of RVP reducing compounds include triethyl amine, tertiary-octyl amine.

[0045] In another embodiment, the oxygenated gasoline includes a blend of gasoline blend stock, one or more suitable oxygenates, and one or more RVP reducing compound including 1-butanol. In yet another embodiment, the oxygenated gasoline is a blend of gasoline blend stock, one or more suitable oxygenates including ethanol, and one or more RVP reducing compounds including 1-butanol.

[0046] Some properties of mixtures of gasoline blend stocks with oxygenate, RVP reducing compounds or both do not vary linearly with the amount each component used. In particular, volatility-related characteristics of such mixtures can diverge from linear proportionality with respect to the amount of each component used. FIG. 3 illustrates how the RVP of a gasoline varies with respect to the volume percent of ethanol in the fuel. FIG. 3 plots the RVP of an unleaded regular gasoline having a base RVP of 6.1 psi as a function of...
the volume percent of ethanol in that gasoline. As shown in FIG. 3, there is a non-linear relationship between the vol % of ethanol and RVP. This non-linear effect has made it particularly difficult to predict the actual impact upon RVP of oxygenates in gasoline. Actual RVP of an oxygenated gasoline varies with the gasoline blend stock used, the particular oxygenate used and the specific concentration of the oxygenate in the oxygenated gasoline. Because of this non-linear variability, RVP of an oxygenated gasoline is determined empirically. RVP data is typically empirically gathered over a range of oxygenate concentrations and over a range of gasoline blend stocks.

[0047] The blend RVP of an oxygenate is typically calculated by measuring the RVP of a fuel before addition of such oxygenate and after addition of such oxygenate. The oxygenate blend RVP values which can be calculated from such empirical data also exhibit non-linear behavior with respect to concentration of the oxygenate in the particular oxygenated gasoline making such blend RVP values difficult to predict. Because of such non-linear effects upon RVP, the calculated blend RVP value is particular to the concentration of a particular oxygenate added to a particular fuel.

[0048] The blend RVP of RVP reducing compounds when calculated as a function of volume fraction of such RVP reducing compound exhibit non-linear behavior making it more difficult to predict the RVP of the resulting mixture. The blend RVP of a suitable RVP reducing compound is typically calculated by measuring the RVP of a fuel before addition of such RVP reducing compound and after addition of such RVP reducing compound. Because RVP reducing compounds exhibit non-linear effect upon RVP when added to a fuel, the measured blend RVP is particular to the concentration of the RVP reducing compound added to the particular fuel.

[0049] We have surprisingly found that the combination of one or more suitable oxygenates and one or more RVP reducing compounds can have a synergistic effect on the RVP value of the gasoline being produced.

[0050] In any embodiment, gasoline blend stock, suitable oxygenates and RVP reducing compounds can be blended in any order. For example, RVP reducing compounds can be added to a mixture including a gasoline blend stock and suitable oxygenates. As another example, one or more suitable oxygenates and one or more RVP reducing compounds can be added in several different locations or in multiple stages. For further examples, RVP reducing compounds can be added with the suitable oxygenates, added before the suitable oxygenates or blended with the suitable oxygenates before being added to a gasoline blend stock. In a preferred embodiment, one or more RVP reducing compounds are added to oxygenated gasoline. In another preferred embodiment, one or more suitable oxygenates and one or more RVP reducing compounds are blended into a gasoline blend stock contemporaneously.

[0051] In any embodiment, more than one suitable oxygenate can be used in place of a single suitable oxygenate and, optionally, more than one RVP reducing compound can be used instead of just one RVP reducing compound. Suitable oxygenates and RVP reducing compounds can be added at any point within the distribution chain. For example, a gasoline blend stock can be transported to a terminal and then suitable oxygenates and RVP reducing compounds can be blended with the gasoline blend stock, individually or in combination, at the terminal. As further example, a gasoline blend stock, one or more suitable oxygenate and one or more RVP reducing compound can be combined at a refinery. Other components or additives can be added at any point in the distribution chain.

[0052] In yet another embodiment, a method for reducing the RVP of an oxygenated gasoline is provided. The method can be practiced at a refinery, terminal, retail site, or any other suitable point in the distribution chain. Preferably, the method is practiced at a terminal already designed for blending ethanol or some other oxygenate with a gasoline blend stock or at a terminal which can be adapted to accommodate such blending.

[0053] According to another embodiment, a gasoline blend stock is blended with either ethanol, another suitable oxygenate, or a combination of suitable oxygenates, and either a RVP reducing compound, or combination of RVP reducing compounds, to produce an oxygenated gasoline fuel having a lower RVP than the oxygenated gasoline without the RVP reducing compounds.

[0054] The particular RVP reducing compound used in any embodiment depends upon the particular gasoline blend stock used and the particular suitable oxygenate used preferably, a RVP reducing compound is chosen such that the blend RVP value of the RVP reducing compound is less than the RVP value of the remaining mixture. More preferably, a RVP reducing compound is selected such that the blend RVP of the RVP reducing compound is at most about 50% of the RVP of the remaining mixture. Alternatively, a RVP reducing compound can be selected such that the blend RVP of the RVP reducing compound is less than about 4.5 psi, more preferably less than about 3.0 psi, more preferably less than about 0.0.

[0055] Regulations for gasoline set limits on various properties of the fuel including, typically, an upper limit on RVP. Such RVP limits may vary with country, region, and season. Such RVP limits place a constraint on the refinery product which can be used as gasoline. Typically, oxygenates, when blended into a gasoline blend stock, will raise the RVP of the resulting blend. Gasoline blend stocks for oxygenate blending typically have an RVP sufficiently below any applicable upper limits to account for the anticipated effect of the oxygenate. This further constrains the refinery product which can be used for gasoline because less high-volatility fuel components can be used for gasoline blend stocks. Such RVP constraint can limit the amount of gasoline available for consumption.

[0056] In another embodiment, a method for reducing the RVP constraint on refinery for the production of gasoline blend stock for oxygenate blending is provided. The RVP constraint on a refinery is lessened because oxygenated gasoline that complies with regulatory RVP limits can be produced using gasoline blend stock which might not otherwise be useable to produce RVP compliant oxygenated gasoline. Another embodiment provides a method to reduce the RVP of an oxygenated gasoline such that some oxygenated gasoline which might not otherwise meet regulatory RVP limits might be further blended to comply with such regulatory RVP limits.

[0057] In yet another embodiment, an oxygenated gasoline is produced by blending a selected gasoline blend stock, a selected suitable oxygenate and a selected RVP reducing compound to form an oxygenated gasoline. The RVP reducing compound reduces the RVP value of the oxygenated gasoline. For a particular suitable oxygenate and particular gasoline blend stock, use of a RVP reducing compound can
allow use of a gasoline blend stock with a higher RVP value than could typically be used to produce an oxygenated gasoline meeting applicable RVP regulations.

[0058] For a given maximum RVP value, a gasoline blend stock, a suitable oxygenate, and a RVP reducing compound are selected such that, even though the RVP value of the mixture of the gasoline blend stock and the suitable oxygenate would exceed the maximum RVP value, the RVP value of the oxygenated gasoline mixture containing the gasoline blend stock, the suitable oxygenate and the RVP reducing compound is less than or equal to the maximum RVP value.

[0059] Without limiting the scope, the following examples illustrate various embodiments of our invention. The specific examples below are discussed in the context of an unleaded gasoline fuel meeting the performance characteristics of ASTM D4814, but it will be appreciated by those in the art that the invention is not limited to such fuel and can be used with any gasoline blend stock or fuel consistent with the description herein.

Comparative Example A

[0060] Several oxygenates were tested for solubility in an unleaded regular gasoline blend stock satisfying the performance characteristics of ASTM D 4814-01a. Solubility was determined at 1 vol % oxygenate compound and at 10 vol % oxygenate compound. The results are shown in Table III below.

<table>
<thead>
<tr>
<th>TABLE III</th>
<th>Solubility in Unleaded Regular Gasoline</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygenate</td>
<td>Compound</td>
</tr>
<tr>
<td>2-propanol</td>
<td>S</td>
</tr>
<tr>
<td>1-butanol</td>
<td>S</td>
</tr>
<tr>
<td>2-butanol</td>
<td>S</td>
</tr>
<tr>
<td>1,3-propanediol</td>
<td>I</td>
</tr>
<tr>
<td>2,3-butanediol</td>
<td>I</td>
</tr>
<tr>
<td>glycerol</td>
<td>I</td>
</tr>
<tr>
<td>acetic acid</td>
<td>S</td>
</tr>
<tr>
<td>ethanol</td>
<td>S</td>
</tr>
</tbody>
</table>

S = Soluble
I = Insoluble

[0061] From the results shown in Table III above, 1,3-propanediol, 2,3-butanediol, and glycerol were insoluble and therefore are not suitable oxygenates for the particular unleaded gasoline product.

Comparative Example B

[0062] The suitable oxygenates from Comparative Example A were tested to determine each compound’s RVP blend value for blending with the unleaded regular gasoline blend stock of Comparative Example A. The RVP of the gasoline blend stock was measured as 8.63 psi as measured in accordance with ASTM D5191. Each oxygenate was blended with the gasoline blend stock at the indicated volume percentage and the RVP of the resulting oxygenated gasoline was measured in the same manner. The particular compounds tested and the volume percent of the materials used are detailed in Table II below. The RVP blend value of the oxygenates for the indicated volume concentration was then calculated and the results set forth in Table IV.

<table>
<thead>
<tr>
<th>TABLE IV</th>
<th>RVP Blend Values (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unleaded Regular Gasoline Blend Stock</td>
<td>Oxygenate</td>
</tr>
<tr>
<td>2-propanol</td>
<td>33.63</td>
</tr>
<tr>
<td>1-butanol</td>
<td>12.63</td>
</tr>
<tr>
<td>2-butanol</td>
<td>8.63</td>
</tr>
<tr>
<td>acetic acid</td>
<td>5.63</td>
</tr>
<tr>
<td>ethanol (not tested)</td>
<td>31.03</td>
</tr>
</tbody>
</table>

[0063] As can be seen by the results in Table IV, the blend RVP values do not linearly correlate with the volume percent of these suitable oxygenate compounds. The suitable oxygenates exhibit an effect upon RVP that is non-linear with respect to the volume percent of the oxygenate compound. The results in Table IV also illustrate that increasing the concentration of different oxygenates can have a different effect upon the particular oxygenate’s blend RVP value. Increasing the concentration of each of 1-butanol, 2-butanol, and acetic acid from 5 vol % to 10 vol % increased the blend RVP value of the oxygenate. However, the same concentration increase for each of 2-propanol and ethanol resulted in a decrease in blend RVP value of the oxygenate.

Example 1

[0064] The gasoline blend stock of Comparative Example A above was blended with 5 vol % suitable oxygenate. Ethanol was used as the suitable oxygenate. The RVP of the resulting oxygenated gasoline was measured to be 9.75 psi when measured in accordance with ASTM D5191. Several potential RVP reducing compounds were blended with the oxygenated gasoline to determine whether the compounds were soluble and to determine the blend RVP value. The blend RVP value was calculated for 1 vol % and 5 vol % blends by measuring the RVP of the resulting gasoline in accordance with ASTM D5191. The results are shown in Table V below.

<table>
<thead>
<tr>
<th>TABLE V</th>
<th>RVP Blend Values (psi)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Unleaded Regular Gasoline with 5 vol % Ethanol</td>
<td>Compound</td>
</tr>
<tr>
<td>2-propanol</td>
<td>−0.25</td>
</tr>
<tr>
<td>1-butanol</td>
<td>−11.25</td>
</tr>
<tr>
<td>2-butanol</td>
<td>−6.25</td>
</tr>
<tr>
<td>1,3-propanediol</td>
<td>1</td>
</tr>
<tr>
<td>2,3-butanediol</td>
<td>8.25</td>
</tr>
<tr>
<td>glycerol</td>
<td>1</td>
</tr>
<tr>
<td>acetic acid</td>
<td>−16.25</td>
</tr>
</tbody>
</table>

I = Insoluble

[0065] Table V illustrates the unpredictable nature of blending oxygenates and RVP reducing compounds with gasoline blend stocks. 1,3-propanediol and glycerol which were insoluble in this particular gasoline blend stock (see Comparative Example A) were also not soluble in the oxygenated gasoline mixture of this Example and therefore are not RVP reducing compounds for this particular mixture. 2,3-butanediol was insoluble in this particular gasoline blend stock (see Comparative Example A), however, it was and is a
RVP reducing compound at 1 vol % when blended with this particular gasoline blend stock and 5 vol % ethanol. 2,3-
butanediol was not soluble, and is not a RVP reducing compound at 5 vol % when blended with this particular gasoline
blend stock and 5 vol % ethanol.

The results set forth in Table V reveal that, surprisingly, some RVP reducing compounds exhibit negative blend
RVP values. Such dramatically low RVP blend values indicate RVP reducing compounds which have a significant
reducing effect upon the RVP of the oxygenated gasoline.

Example 2

The gasoline blend stock of Comparative Example A above was blended with 10 vol % of a suitable oxygenate.
Ethanol was used as the suitable oxygenate. The RVP of the resulting oxygenated gasoline was measured to be 9.75 psi
when measured in accordance with ASTM D5191. Several potential RVP reducing compounds were blended with the
oxygenated gasoline and the blend RVP value was calculated for 1 vol % and 5 vol % blends by measuring the RVP of the
resulting mixture in accordance with ASTM D5191. The results are shown in Table VI below.

<table>
<thead>
<tr>
<th>Potential RVP</th>
<th>Unleaded Regular Gasoline with 10 vol % Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound</td>
<td>1%</td>
</tr>
<tr>
<td>2-propanol</td>
<td>-5.25</td>
</tr>
<tr>
<td>1-butanol</td>
<td>-8.25</td>
</tr>
<tr>
<td>2-butanol</td>
<td>-6.25</td>
</tr>
<tr>
<td>1,3-propanediol</td>
<td>-9.25</td>
</tr>
<tr>
<td>2,3-butanediol</td>
<td>-3.25</td>
</tr>
<tr>
<td>glycerol</td>
<td>1</td>
</tr>
<tr>
<td>acetic acid</td>
<td>-8.25</td>
</tr>
</tbody>
</table>

1 = iso-tributyl

Table VI further illustrates the unpredictable nature of blending oxygenates and RVP reducing compounds with
gasoline blend stocks. 1,3-propanediol was not a suitable RVP reducing compound for the oxygenated gasoline mixture
of Example 1, but is a suitable RVP reducing compound at 1 vol % for the oxygenated gasoline mixture of this
example. Similarly, 2,3-butanediol was not a suitable RVP reducing compound at 5 vol % in the oxygenated gasoline
mixture of Example 1, but is a suitable RVP reducing compound at 5 vol % for the oxygenated gasoline mixture of this
example.

The results in Table VI also reveal that these RVP reducing compounds at 1 vol % exhibited negative RVP blend
values. Even at 5 vol % concentration, the RVP reducing compounds exhibited RVP blend values below 2.0 psi. Such
RVP blend values indicate significant RVP reducing effect.

The examples above show how RVP reducing compounds can reduce the RVP of an oxygenated gasoline. In
regions which have a maximum RVP limit, refiners typically produce gasoline blend stocks significantly below such
limit in anticipation of an RVP increase from oxygenate blending. Because a suitable RVP reducing compound can be
used to reduce the RVP of an oxygenated gasoline, refiners can utilize gasoline blend stocks to produce oxygenated gaso-
lines which comply with applicable RVP limits which gasoline blend stocks might not otherwise be usable to produce
RVP compliant oxygenated gasoline.

That which is claimed is:
1. A gasoline composition comprising:
a gaso line blend stock;
an oxygenate selected from the group consisting of alco-
hols, ketones, esters, aldehydes, carboxylic acids, ethers, ether alcohols, and poly alcohols present at from
about one percent (1%) to about ten percent (10%) by volume to form a gasoline-oxygenate blend; and
isobutanol produced from biomass present at from about
one percent (1%) to about five percent (5%) by volume
to form a gasoline-oxygenate-isobutanol blend, wherein the difference between the infrared absorbance spec-
trum of the gasoline-oxygenate blend and the infrared absorbance spectrum of the gasoline-oxygenate-isobu-
tanol blend falls within a ratio corresponding to a pre-
determined Reid Vapor Pressure (RVP) value limit.
2. The gasoline composition of claim 1, wherein the isobu-
tanol has a RVP blend value less than about zero point zero
pounds per square inch (0.0 psi).
3. The gasoline composition of claim 1, wherein the gaso-
l ine-oxygenate blend’s RVP value is at least about six point
nine pounds per square inch (6.9 psi).
4. The gasoline composition of claim 1, wherein the gaso-
l ine-oxygenate blend has a normalized relative absorbance
greater than about zero point zero five (0.05).
5. The gasoline composition of claim 4, wherein the gaso-
l ine-oxygenate-isobutanol blend has a normalized relative absorbance less than about zero point four five (0.045).
6. The gasoline composition of claim 1, wherein the oxy-
genate comprises ethanol.
7. The gasoline composition of claim 1, wherein the dif-
ference between the infrared absorbance spectrum of the gasoline-oxygenate blend and the infrared absorbance spec-
trum of the gasoline-oxygenate-isobutanol blend indicates a synergistic RVP reduction in comparison to the gaso-
l ine-oxygenate blend.
8. The gasoline composition of claim 1, wherein the gaso-
l ine-oxygenate-isobutanol blend exhibits a normalized relative absorbance associated with a synergistic RVP reduction
from three-thousand six-hundred eighty reciprocal centimeters (3680 cm\(^{-1}\)) to three-thousand one-hundred reciprocal
centimeters (3100 cm\(^{-1}\)).
9. A method of reducing the RVP of a gasoline blend stock
in the production of oxygenated gasolines having a predetermined maximum RVP limit comprising:
providing a gasoline blend stock;
adding at least about one percent (1%) to about ten percent
(10%) by volume of one oxygenate selected from the group consisting of alcohols, ketones, esters, aldehydes,
carboxylic acids, ethers, other alcohols and poly alcohols to form a gasoline-oxygenate blend;
measuring the infrared absorbance spectrum of the gaso-
l ine-oxygenate blend;
reducing the RVP of the gasoline-oxygenate blend by add-
l ing isobutanol to form a gasoline-oxygenate-isobutanol blend;
measuring the infrared absorbance spectrum of the gaso-
l ine-oxygenate-isobutanol blend; and
repeating the reducing and the measuring the infrared
absorbance spectrum of the gasoline-oxygenate-isobu-
tanol blend until a difference spectrum for the gasoline-
oxygenate-isobutanol blend falls within a ratio corresponding to a predetermined RVP limit.

10. The method of claim 9, further comprising using empirically gathered RVP data for isobutanol over a range of oxygenate concentrations and a range of gasoline blend stocks to determine the gasoline-oxygenate blend's RVP.

11. A method of reducing Reid Vapor Pressure (RVP) constraint on a gasoline blend stock for production of oxygenated gasolines with a predetermined maximum RVP limit comprising:
   providing a gasoline blend stock;
   reducing the gasoline blend stock's RVP by adding isobutanol to the gasoline blend stock to form a gasoline-isobutanol blend;
   measuring the gasoline-isobutanol blend's infrared absorbance spectrum;
   adding an oxygenate selected from the group consisting of alcohols, ketones, esters, aldehydes, carboxylic acids, ethers, ether alcohols, and poly alcohols to form a gasoline-isobutanol-oxygenate blend;
   measuring the gasoline-isobutanol-oxygenate blend's infrared absorbance spectrum; and
   repeating the adding and the measuring the infrared absorbance spectrum of the gasoline-isobutanol-oxygenate blend until a difference between the infrared absorbance spectrum for the gasoline-isobutanol blend and the infrared absorbance spectrum for the gasoline-isobutanol-oxygenate blend falls within a ratio corresponding to a predetermined RVP limit.

12. The method of claim 11, wherein the oxygenate and isobutanol are added in different locations.

13. The method of claim 11, further comprising using empirically gathered RVP data to determine the RVP of a gasoline blend that includes the oxygenate.

14. A method of blending oxygenated gasoline to meet a predetermined Reid Vapor Pressure (RVP) limit comprising:
   providing a gasoline blend stock;
   measuring an infrared absorbance spectrum of the gasoline stock;
   adding a pre-blend of isobutanol and at least one oxygenate selected from the group consisting of alcohols, ketones, esters, aldehydes, carboxylic acids, ethers, ether alcohols, and poly alcohols to form a gasoline-isobutanol-oxygenate blend;
   measuring an infrared absorbance spectrum of the gasoline-isobutanol-oxygenate blend; and
   repeating the adding and the measuring an infrared absorbance spectrum of the gasoline-isobutanol-oxygenate blend until a difference between the infrared absorbance spectrum of the gasoline-isobutanol-oxygenate blend and the infrared absorbance spectrum of the gasoline blend stock falls within a ratio corresponding to a predetermined RVP limit.

15. The method of claim 14, wherein the oxygenate and isobutanol are added in different locations.

16. The method of claim 14, further comprising using empirically gathered RVP data for isobutanol over a range of concentrations for oxygenate and gasoline blend stocks to determine a RVP for a gasoline blend that includes the oxygenate.

17. A gasoline composition comprising:
   (a) a gasoline blend stock;
   (b) ethanol present at from about one percent (1%) to about ten percent (10%) by volume to form a gasoline-oxygenate blend; and
   (c) isobutanol produced from biomass present at from about one percent (1%) to about five percent (5%) by volume to form a gasoline-oxygenate-isobutanol blend, wherein the difference between the infrared absorbance spectrum of the gasoline-oxygenate blend and the infrared absorbance spectrum of the gasoline-oxygenate-isobutanol blend falls within a ratio corresponding to a predetermined RVP value limit.

18. The gasoline composition of claim 17, wherein the difference between the infrared absorbance spectrum of the gasoline-oxygenate blend and the infrared absorbance spectrum of the gasoline-oxygenate-isobutanol blend indicates a synergistic RVP reduction in comparison to the gasoline-oxygenate blend.

19. The gasoline composition of claim 17, wherein the isobutanol has a RVP blend value less than about zero point zero pounds per square inch (0.0 psi).

20. The gasoline composition of claim 17, wherein the gasoline-oxygenate-isobutanol blend is associated with a normalized absorbance spectrum from three-thousand six-hundred eighty reciprocal centimeters (3680 cm⁻¹) to three-thousand one-hundred reciprocal centimeters (3100 cm⁻¹) that identifies the synergistic RVP reduction.

21. A gasoline composition comprising:
   an oxygenate gasoline blend in which the oxygenate comprises from about one percent (1%) to about ten percent (10%) by volume in the oxygenate gasoline blend; and
   isobutanol that is produced from biomass and exhibits a synergistic Reid Vapor Pressure (RVP) reduction associated with a normalized absorbance in band areas from three-thousand six-hundred eighty reciprocal centimeters (3680 cm⁻¹) to three-thousand one-hundred reciprocal centimeters (3100 cm⁻¹) in a blend with the oxygenate gasoline in comparison to the gasoline included in the oxygenate gasoline blend.

22. The gasoline composition of claim 21, wherein the oxygenate comprises ethanol.

23. The gasoline composition of claim 21, wherein oxygenate is selected from the group consisting of alcohols, ketones, esters, aldehydes, carboxylic acids, ethers, ether alcohols, and poly alcohols.

24. The gasoline composition of claim 21, wherein the oxygenate comprises an oxygenate that increases the gasoline composition's RVP over that of the gasoline included in the oxygenate gasoline blend.