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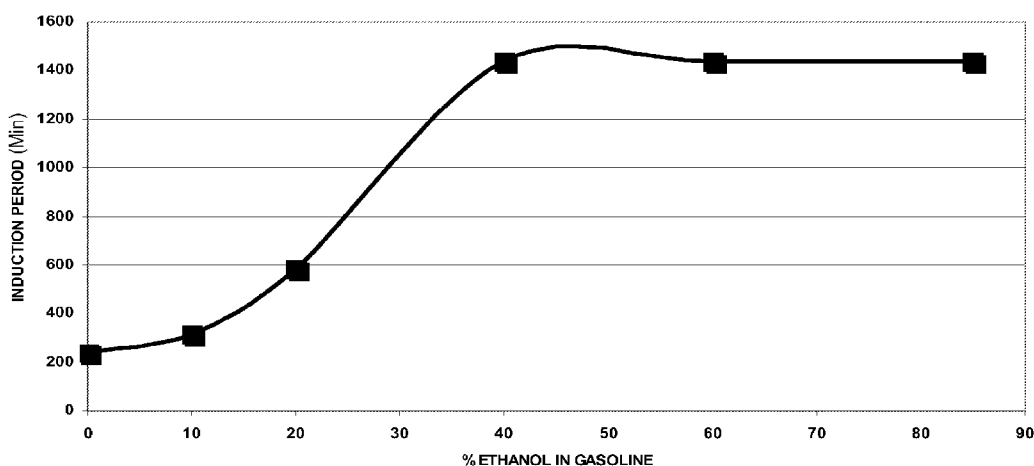
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(54) Title: GASOLINE FUEL COMPOSITIONS HAVING INCREASED OXIDATIVE STABILITY



(57) Abstract: The present invention relates to gasoline or a gasoline and ethanol blend fuel compositions that have improved oxidation stability. More specifically, the gasoline or a gasoline and ethanol blend fuel compositions include at least one antioxidant that increases the oxidative stability of the fuel. The gasoline or a gasoline and ethanol blend fuel compositions may also include an antioxidant mixture, or an antioxidant mixture in combination with a polar and/or nonpolar solvent, that increases the oxidative stability of the fuel.

WO 2007/103675 A2

## GASOLINE FUEL COMPOSITIONS HAVING INCREASED OXIDATIVE STABILITY

### FIELD OF THE INVENTION

[0001] The present invention relates to gasoline or a gasoline and ethanol blend fuel compositions that have improved oxidation stability. More specifically, the gasoline and ethanol blend fuel compositions include at least one antioxidant that increases the oxidative stability of the fuel.

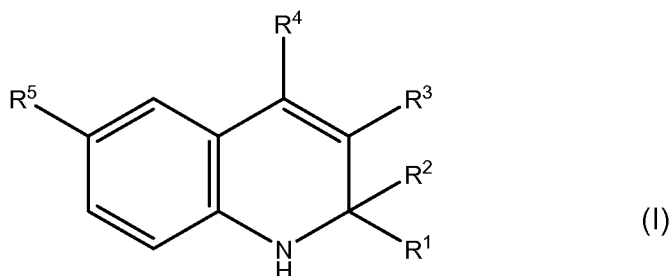
### BACKGROUND OF THE INVENTION

[0002] Gasoline and gasoline and ethanol blends compositions are typically used as fuels for internal combustion engines. Various processes including a catalytic cracking process from crude oil and a catalytic reforming process from low-octane naphthas may be utilized to produce gasoline. Gasoline fuels, despite their method of production, easily oxidize in the presence of oxygen, UV light, and heat. The products formed from this oxidation give rise to sediment or gum formation within the fuel and may cause corrosion and plugging of internal combustion engines.

[0003] As such, there is a need for a gasoline or gasoline and ethanol blend composition having improved oxidation stability that reduces or eliminates sedimentation and gum formation within the fuel and concomitantly, reduces or eliminates corrosion or plugging of internal combustion engines.

### SUMMARY OF THE INVENTION

[0004] One aspect of the present invention provides a fuel composition. The fuel composition comprises gasoline; ethanol; and an antioxidant comprising Formula (I):



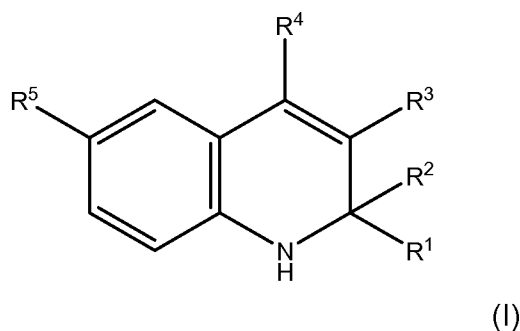
wherein:

$R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are independently selected from the group consisting of hydrogen and an alkyl group having from 1 to about 6 carbons;

$R^5$  is an alkoxy group having from 1 to about 12 carbons.

[0005] Yet another aspect of the invention encompasses a fuel composition comprising gasoline in an amount ranging from about 60% to about 99% by weight of the composition; ethanol in an amount ranging from about 1% to about 40% by weight of the composition; and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline in an amount ranging from about 20 to about 1500 ppm.

[0006] A further aspect of the invention provides a method for increasing the oxidative stability of a fuel composition comprising gasoline and ethanol. The method comprises contacting the fuel composition with an antioxidant comprising Formula (I):



wherein:

$R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are independently selected from the group consisting of hydrogen and an alkyl group having from 1 to about 6 carbons;

$R^5$  is an alkoxy group having from 1 to about 12 carbons.

[0007] Other aspects and iterations of the invention will be in part apparent and in part pointed out hereinafter.

## FIGURES

[0008] **Figure 1** is a graph depicting the effect of ethanol on the induction period of gasoline compositions. Plotted is the induction time versus the amount of ethanol in each gasoline formulation.

[0009] **Figure 2** is a graph depicting effect of ethoxyquin (labeled as ETQ) on the induction period of ethanol free gasoline.

[0010] **Figure 3** is a graph depicting the effect of ethoxyquin (ETQ) and ethanol (ETOH) on the induction period. Plotted is the induction period in minutes versus level of ethoxyquin in ppm.

## **DETAILED DESCRIPTION OF THE INVENTION**

[0011] The present invention provides gasoline fuel compositions that have improved oxidative stability. Typically, the gasoline fuel compositions comprise gasoline, at least one antioxidant that increases gasoline stability, and optionally, ethanol. In addition to improved oxidative stability, the gasoline fuel compositions also may have longer induction times, lower amounts of insolubles, and lower peroxide values. Advantageously, the gasoline fuel compositions may also have lower NO<sub>x</sub> and CO<sub>2</sub> emissions.

### ***I. Gasoline***

[0012] The fuel composition of the invention includes gasoline. Gasoline suitable for use in the invention is typically a petroleum-derived liquid mixture consisting mostly of hydrocarbons used as fuel in internal combustion engines. The hydrocarbons forming the gasoline generally consist of between 5 to about 12 carbon atoms per molecule. A typical gasoline may include a mixture of paraffins, naphthenes, aromatics, and olefins. The ratios of these components forming gasoline suitable for use in the invention can and will vary depending on a variety of factors, such as, the oil refining process, the crude oil used, and the grade of gasoline.

[0013] Exemplary gasoline formulations will generally have a relatively high octane rating. The gasoline composition, for example, may have an octane rating of greater than about 85%, about 86%, about 87%, about 88%, about 89%, about 90%, about 91%, about 92%, about 93%, about 94%, about 95%, about 96%, about 97%, about 98%, about 99%, or about 100%. Octane rating may be measured by any method generally known in the art, such as by the Research Octane Number (i.e., RON). Generally speaking, in this method octane rating of gasoline is typically measured relative to a mixture of isooctane (i.e., 2,2,4-

trimethylpentane) and n-heptane by running the fuel samples through a specific test engine with a variable compression ratio under controlled conditions. By way of example, an 87-octane gasoline typically has the same octane rating as a mixture of 87% (v/v) isooctane and 13% (v/v) n-heptane.

[0014] A variety of methods known in the art may be used to make the gasoline of the present invention. The gasoline may be produced through a catalytic cracking process from crude oil. As used herein, a catalytic cracking process is defined as a refining process by which certain crude cuts are broken down or "cracked" into simpler hydrocarbon compounds at the molecular level by means of extreme heat, pressure, and exposure to a chemical catalyst. Alternatively, gasoline may be produced by a catalytic reforming process. A variety of catalytic reforming processes are suitable to produce gasoline, including but not limited to, platforming, powerforming, ultraforming, and Thermoform catalytic reforming. Generally, in a catalytic reforming process low-octane naphthas are subjected to a high temperatures and relatively mild hydrogen partial pressures in the presence of multinuclear catalysts, such as platinum, or rhenium, or on a carrier such as zeolites. During the process, the naphtha feedstock, mainly consisting of paraffins, undergoes numerous reactions including hydrogenation, alkylation, polymerization, cracking, cyclization, isomerization, among others. The process produces light paraffinic gases (LPG), hydrogen, and the aromatic and naphthenic compounds that make up the backbone of high-octane gasoline, such as benzene, toluene, cyclopentane, cyclohexane, and ethyl-benzene, among others. Alternatively, the gasoline may be purchased from a commercially available source.

## ***II. Ethanol***

[0015] The present invention also contemplates fuels that are blends of gasoline and ethanol. Generally speaking, ethanol, also known as ethyl alcohol or grain alcohol, is used as fuel or as an octane-boosting, pollution-reducing additive to gasoline.

[0016] The ethanol may be present in a gasoline ethanol mixture in an amount ranging from about 0% to about 5%, from about 5% to about 10%, from about 10% to about 15%, from about 15% to about 20%, from about 20% to about

25%, from about 25% to about 30%, from about 30% to about 35%, from about 35% to about 40%, from about 40% to about 45%, from about 45% to about 50%, from about 50% to about 55%, from about 55% to about 60%, from about 60% to about 65%, from about 65% to about 70%, from about 70% to about 75%, from about 75% to about 80%, from about 80% to about 85%, from about 85% to about 90%, from about 90% to about 95%, or greater than about 95% by weight of the composition. Exemplary compositions may include ethanol in an amount ranging from about 5% to about 10%, from about 10% to about 15%, from about 15% to about 20%, from about 20% to about 25%, from about 25% to about 30%, from about 30% to about 35%, or less than 40% by weight of the composition.

[0017] Ethanol may be produced using a variety of feedstocks. For example, ethanol may be produced from biomass or crops. In one embodiment, the ethanol is produced from a crop. Suitable crops for ethanol production include corn, milo, sorghum, wheat, barley, potatoes, sugarcane, hemp, kenaf, sugar beets, barley, cassava, sunflower, seaweed, and eucalyptus. It is, however, envisioned that other crops may also be used without departing from the scope of the invention. In another embodiment, the ethanol is produced from biomass. Suitable biomass for ethanol production may include farm wastes, agricultural forestry residues, industrial waste, municipal waste, trees, grasses, sugarcane residues, rice hulls, paper mill wastes, molasses, and other organic or cellulose materials. In yet another embodiment, the ethanol is produced from a plant-derived, cellulose material. Suitable plant-derived, cellulose materials include switchgrass, corncobs, wheat straw, corn stover, and sawdust. As will be appreciated by the skilled artisan, ethanol may also be produced from a combination of different sources. In an exemplary embodiment, the ethanol is produced from a source selected from the group consisting of corn, grain sorghum, wheat, barley, potatoes, sugar cane, plant-derived cellulose material, and biomass. In a further exemplary embodiment, the ethanol is produced from corn. In another exemplary embodiment, the ethanol is produced from a plant-derived cellulose material.

[0018] Several methods generally known in the art may be used to produce ethanol without departing from the scope of the invention. In general, ethanol may be produced by chemical synthesis or biological fermentation. Chemical synthesis involves the hydrolysis of ethylene obtained from coal

gasification or other mineral livestock. This method is generally used for low volume applications that need unusually high purity, anhydrous ethanol and fills a niche market found in the chemical industry. Fermentation for the production of ethanol utilizes microorganisms, most commonly yeast, for the conversion of sugars to alcohols. This process occurs in the absence of oxygen forcing the microorganisms to utilize an anaerobic metabolic pathway. This pathway converts sugars into ethanol, carbon dioxide, chemical energy, and kinetic (heat) energy. Typically, a dry mill process produces fuel grade ethanol from grains. Such a process typically includes milling, liquefaction, saccharification, fermentation, distillation, dehydration, and denaturing. Another embodiment that may be used to produce ethanol includes contacting a biomass with genetically engineered *Escherichia Coli* strains, as disclosed in U.S. Patent No. 5,000,000, herein incorporated by reference. Alternatively, the ethanol may be purchased from a commercially available source.

## **II. Antioxidants**

[0019] The gasoline composition of the invention also includes one or more antioxidants. Suitable antioxidants for use in the present invention substantially inhibit the oxidation process and thus, enhance the fuel composition's oxidative stability. Methods for measuring oxidative stability of a gasoline composition are described in more detail below, and in particular, in the Examples.

### **(a) individual antioxidants**

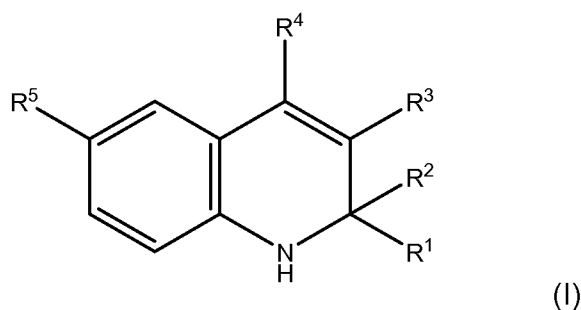
[0020] Those skilled in the art will appreciate that several suitable antioxidants may be used depending on the type of fuel to be stabilized. In one embodiment, the antioxidant may be selected from the group comprising of hindered amines, such as diphenyl amines; butylated hydroxyanisole; butylated hydroxytoluene; gallates such as octyl gallate, dodecyl gallate, and 3,4,5-trihydroxybenzoic acid n-propyl ester (propyl gallate); 1,2,3-trihydroxybenzene (pyrogallol); fatty acid esters including, but not limited to, methyl esters such as methyl linoleate, methyl oleate, methyl stearate, 2,2,6,6-tetramethylpiperidinoxyl, also referred to as tanan; 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl, also referred to as tanol; dimethyl-p-phenylaminophenoxysilane; di-p-anisylazoxides; p-

hydroxydiphenylamine, and carbonates, phthalates, and adipates thereof; and diludin, a 1,4-dihydropyridine derivative.

[0021] In another embodiment, the antioxidant may be selected from the group comprising oil-soluble antioxidants, including, but not limited to ascorbyl palmitate, butylated hydroxyanisole, butylated hydroxytoluene, phenyl-alpha-naphthylamine, and hydroquinone.

[0022] In a further embodiment, the antioxidant may be a synthetic antioxidants selected from the phenolic acids and derivatives; 2-tert-butylhydroquinone (TBHQ); mixtures of TBHQ and 2-tertiarybutyl-4-hydroxyanisole; 3-tertiarybutyl-4-hydroxyanisole; 2,6-di-tert-butyl-4-hydroxymethylphenol; 2-6-di-tert-butyl-4-methylphenol (BHT) and t-tert-butyl-4-methylphenol (t-BHT); 2-ter-butyl-4-methoxyphenol (BHA); mono tertiary butyl hydroquinone, di-tert-butyl hydroquinone, polyphosphates; trihydroxy butyrophenone; anoxomer; and combinations thereof. Other suitable synthetic antioxidants include the antioxidants marketed under the names VANLUBE, IONOL, and BAYNOX.

[0023] In another embodiment, the antioxidant may be a quinoline or a substituted quinoline. In an exemplary embodiment, the quinoline is a substituted 1,2-dihydroquinoline compound. Substituted 1,2-dihydroquinoline compounds suitable for use in the invention may correspond to formula (I):



wherein:

$R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are independently selected from the group consisting of hydrogen and an alkyl group having from 1 to about 6 carbons;

$R^5$  is an alkoxy group having from 1 to about 12 carbons.

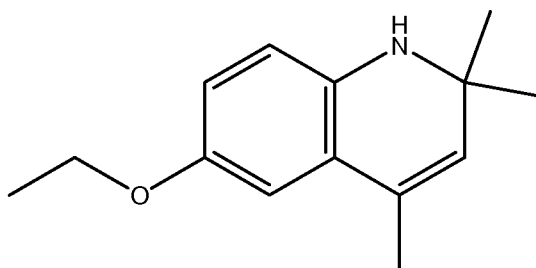
[0024] In another embodiment, the substituted 1,2-dihydroquinoline will have formula (I) wherein:



$R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are independently selected from the group consisting of hydrogen and an alkyl group having from 1 to about 4 carbons; and

$R^5$  is an alkoxy group having from 1 to about 4 carbons.

[0025] An exemplary substituted 1,2-dihydroquinoline is 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline having the formula:



6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, commonly known as ethoxyquin, is sold under the trademark SANTOQUIN<sup>®</sup> (by Novus International Inc. of Saint Louis Missouri). The present invention also encompasses salts of ethoxyquin and other compounds having formula (I). Ethoxyquin and other compounds having formula (I) may be purchased commercially from Novus International, Inc. or made in accordance with methods generally known in the art, for example, as detailed in U.S. Patent No. 4,772,710, which is hereby incorporated by reference in its entirety.

#### (b) antioxidant formulations

[0026] The antioxidant may be a blend of any of the antioxidants detailed in II(a). For example, the antioxidant may include, two, three, four, five or more of any of the aforementioned antioxidants. In an exemplary embodiment, the antioxidant blend will include a compound having formula (I). Non-limiting examples of suitable antioxidant blends are detailed in **Table A**.

TABLE A	
First Antioxidant	Second Antioxidant or Antioxidant Mixture
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	2-tert-butylhydroquinone

TABLE A	
First Antioxidant	Second Antioxidant or Antioxidant Mixture
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	3,4,5-trihydroxybenzoic acid n-propyl ester
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	1,2,3-trihydroxybenzene
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	2-tert-butyl-4-hydroxyanisole
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	t-tert-butyl-4-methylphenol
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	dodecyl gallate
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	octyl gallate
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	2-tert-butylhydroquinone and 3,4,5-trihydroxybenzoic acid n-propyl ester
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	2-tert-butylhydroquinone and 1,2,3-trihydroxybenzene
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	1,2,3-trihydroxybenzene and 2-tert-butyl-4-hydroxyanisole
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	1,2,3-trihydroxybenzene and t-tert-butyl-4-methylphenol
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	1,2,3-trihydroxybenzene and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	1,2,3-trihydroxybenzene and dodecyl gallate
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	1,2,3-trihydroxybenzene and octyl gallate
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	3,4,5-trihydroxybenzoic acid n-propyl ester and 1,2,3-trihydroxybenzene
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	3,4,5-trihydroxybenzoic acid n-propyl ester and 2-tert-butyl-4-hydroxyanisole
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	3,4,5-trihydroxybenzoic acid n-propyl ester and t-tert-butyl-4-methylphenol
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	3,4,5-trihydroxybenzoic acid n-propyl ester and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	3,4,5-trihydroxybenzoic acid n-propyl ester and dodecyl gallate
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	3,4,5-trihydroxybenzoic acid n-propyl ester and octyl gallate
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	1,2,3-trihydroxybenzene and 2-tert-butyl-4-hydroxyanisole
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	1,2,3-trihydroxybenzene and t-tert-butyl-4-methylphenol
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	1,2,3-trihydroxybenzene and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene

TABLE A	
First Antioxidant	Second Antioxidant or Antioxidant Mixture
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	1,2,3-trihydroxybenzene and dodecyl gallate
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	1,2,3-trihydroxybenzene and octyl gallate
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	2-tert-butyl-4-hydroxyanisole and dodecyl gallate
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	2-tert-butyl-4-hydroxyanisole and t-tert-butyl-4-methylphenol
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	2-tert-butyl-4-hydroxyanisole and octyl gallate
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	t-tert-butyl-4-methylphenol and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	t-tert-butyl-4-methylphenol and dodecyl gallate
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	t-tert-butyl-4-methylphenol and octyl gallate
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and dodecyl gallate
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and octyl gallate
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	dodecyl gallate and octyl gallate
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and 2-tert-butylhydroquinone
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	2-tert-butylhydroquinone and paraffin oil
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and paraffin oil
6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline	2-tert-butylhydroquinone, 1,2-Propanediol, and paraffin oil

### (c) solvents

[0027] The antioxidant composition may further comprise a polar solvent or a non-polar solvent. Generally speaking, a polar solvent may be utilized to solubilize any of the antioxidants that are water-soluble and the non-polar solvent may be utilized to solubilize hydrophobic antioxidants. Suitable examples of polar solvents include, but are not limited to, alcohols such as methanol, glycerol,

isopropyl alcohol, ethyl alcohol, propylene glycol, erythritol, xylitol, sorbitol, maltitol, mannitol, water, or combinations thereof. In one embodiment, the polar solvent is glycerol. In another embodiment, the polar solvent is propylene glycol. Other suitable solvents include hexane, xylene, octane, and paraffins. The concentration of the solvent will vary depending upon the combination of antioxidants in the composition. In general, the percent by volume of the solvent may range from about 5% to about 50%. The percent by volume of glycerol may be about 5%, 10%, 15%, 20%, or 25%. The percent by volume of propylene glycol may be about 5%, 10%, 15%, 20%, or 25%.

### **III. Fuel Compositions**

[0028] The invention provides several suitable combinations of gasoline, ethanol, and antioxidants. In one alternative, the fuel composition may comprise gasoline and one antioxidant. In another alternative, the fuel composition may comprise gasoline, ethanol, and one antioxidant. In yet a further alternative, the fuel composition may comprise gasoline and at least two antioxidants. In this embodiment, the fuel composition may be gasoline in combination with any of the antioxidants described in Part II other than 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline. Suitable combinations of each type of fuel composition are detailed below.

#### **(a) Fuel Composition with Gasoline and One Antioxidant**

[0029] Examples of exemplary fuel compositions having gasoline and one antioxidant are presented in Table 1 below. Alternatively, each fuel composition detailed in Table 1 may also include 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline.

TABLE 1	
<b>Fuel</b>	<b>Antioxidants</b>
Gasoline	2-tert-butylhydroquinone
Gasoline	3,4,5-trihydroxybenzoic acid n-propyl ester
Gasoline	1,2,3-trihydroxybenzene
Gasoline	2-tert-butyl-4-hydroxyanisole
Gasoline	t-tert-butyl-4-methylphenol
Gasoline	2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
Gasoline	dodecyl gallate

TABLE 1	
Fuel	Antioxidants
Gasoline	octyl gallate

**(b) Fuel Composition with Gasoline, Ethanol and One Antioxidant**

[0030] In another embodiment, the fuel composition of the invention comprises a blend of gasoline, ethanol, and one antioxidant that increases the oxidative stability of the fuel composition. In this embodiment, the fuel composition may be any of the ethanol described in Part I in combination with a gasoline and any of the antioxidants described in Part II. Generally speaking, the fuel composition may comprise from about 15% to about 95% by weight gasoline and from about 5% to about 85% by weight ethanol. In another embodiment, the fuel composition may comprise from about 80% to about 95% by weight gasoline and from about 5% to about 20% by weight ethanol. In an alternative embodiment, the fuel composition may comprise from about 90% to about 95% by weight gasoline and from about 5% to about 10% by weight ethanol. Examples of exemplary fuel compositions are presented in Table 2 below. Alternatively, each fuel composition detailed in Table 2 may also include 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline.

TABLE 2		
Fuel	Ethanol Fuel Raw Material	Antioxidants
Gasoline	Corn	2-tert-butylhydroquinone
Gasoline	Corn	3,4,5-trihydroxybenzoic acid n-propyl ester
Gasoline	Corn	1,2,3-trihydroxybenzene
Gasoline	Corn	2-tert-butyl-4-hydroxyanisole
Gasoline	Corn	t-tert-butyl-4-methylphenol
Gasoline	Corn	2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
Gasoline	Corn	dodecyl gallate
Gasoline	Corn	octyl gallate
Gasoline	Plant-derived cellulose material	2-tert-butylhydroquinone
Gasoline	Plant-derived cellulose material	3,4,5-trihydroxybenzoic acid n-propyl ester
Gasoline	Plant-derived cellulose material	1,2,3-trihydroxybenzene

TABLE 2		
Fuel	Ethanol Fuel Raw Material	Antioxidants
Gasoline	Plant-derived cellulose material	2-tert-butyl-4-hydroxyanisole
Gasoline	Plant-derived cellulose material	t-tert-butyl-4-methylphenol
Gasoline	Plant-derived cellulose material	2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
Gasoline	Plant-derived cellulose material	dodecyl gallate
Gasoline	Plant-derived cellulose material	octyl gallate
Gasoline	Sugarcane	2-tert-butylhydroquinone
Gasoline	Sugarcane	3,4,5-trihydroxybenzoic acid n-propyl ester
Gasoline	Sugarcane	1,2,3-trihydroxybenzene
Gasoline	Sugarcane	2-tert-butyl-4-hydroxyanisole
Gasoline	Sugarcane	t-tert-butyl-4-methylphenol
Gasoline	Sugarcane	2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
Gasoline	Sugarcane	dodecyl gallate
Gasoline	Sugarcane	octyl gallate
Gasoline	Grain sorghum	2-tert-butylhydroquinone
Gasoline	Grain sorghum	3,4,5-trihydroxybenzoic acid n-propyl ester
Gasoline	Grain sorghum	1,2,3-trihydroxybenzene
Gasoline	Grain sorghum	2-tert-butyl-4-hydroxyanisole
Gasoline	Grain sorghum	t-tert-butyl-4-methylphenol
Gasoline	Grain sorghum	2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
Gasoline	Grain sorghum	dodecyl gallate
Gasoline	Grain sorghum	octyl gallate
Gasoline	Wheat	2-tert-butylhydroquinone
Gasoline	Wheat	3,4,5-trihydroxybenzoic acid n-propyl ester
Gasoline	Wheat	1,2,3-trihydroxybenzene
Gasoline	Wheat	2-tert-butyl-4-hydroxyanisole
Gasoline	Wheat	t-tert-butyl-4-methylphenol
Gasoline	Wheat	2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
Gasoline	Wheat	dodecyl gallate
Gasoline	Wheat	octyl gallate
Gasoline	Barley	2-tert-butylhydroquinone
Gasoline	Barley	3,4,5-trihydroxybenzoic acid n-propyl ester
Gasoline	Barley	1,2,3-trihydroxybenzene
Gasoline	Barley	2-tert-butyl-4-hydroxyanisole
Gasoline	Barley	t-tert-butyl-4-methylphenol

TABLE 2		
Fuel	Ethanol Fuel Raw Material	Antioxidants
Gasoline	Barley	2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
Gasoline	Barley	dodecyl gallate
Gasoline	Barley	octyl gallate
Gasoline	Potatoes	2-tert-butylhydroquinone
Gasoline	Potatoes	3,4,5-trihydroxybenzoic acid n-propyl ester
Gasoline	Potatoes	1,2,3-trihydroxybenzene
Gasoline	Potatoes	2-tert-butyl-4-hydroxyanisole
Gasoline	Potatoes	t-tert-butyl-4-methylphenol
Gasoline	Potatoes	2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
Gasoline	Potatoes	dodecyl gallate
Gasoline	Potatoes	octyl gallate
Gasoline	Biomass	2-tert-butylhydroquinone
Gasoline	Biomass	3,4,5-trihydroxybenzoic acid n-propyl ester
Gasoline	Biomass	1,2,3-trihydroxybenzene
Gasoline	Biomass	2-tert-butyl-4-hydroxyanisole
Gasoline	Biomass	t-tert-butyl-4-methylphenol
Gasoline	Biomass	2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
Gasoline	Biomass	dodecyl gallate
Gasoline	Biomass	octyl gallate

[0031] In one preferred embodiment, the fuel composition comprises a gasoline, an ethanol produced from corn, and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline. In another preferred embodiment, the fuel composition comprises a gasoline, an ethanol produced from sugarcane, and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline. In yet another preferred embodiment, the fuel composition comprises a gasoline, an ethanol produced from a plant-derived, cellulose material and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline. In another preferred embodiment, the fuel composition comprises a gasoline, an ethanol produced from a biomass, and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline. Those skilled in the art will appreciate that the concentration of antioxidants added to the gasoline and ethanol blend can and will vary depending on the source of ethanol. In one embodiment, the fuel composition comprises a gasoline, an ethanol produced from a plant-derived, cellulose material, and from about 20 ppm to about 1500 ppm of 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline. In another embodiment, the fuel composition comprises a gasoline, an ethanol produced from corn, and from about 50 ppm to about 500 ppm of 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline.

**(c) Fuel Composition with Gasoline and at least two Antioxidants**

[0032] The present invention is also directed to a fuel composition comprising a gasoline and an antioxidant mixture comprising at least two antioxidants. In one embodiment, the fuel composition comprises the gasoline as described in Part I and an antioxidant mixture comprising at least two antioxidants as described in Part II of the specification above. Of course those skilled in the art will appreciate that the antioxidant mixtures will vary considerably depending on the desired stabilization of the gasoline. Examples of exemplary fuel compositions are presented in Table 3 below.

TABLE 3	
Fuel	Antioxidants
Gasoline	2-tert-butylhydroquinone and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline
Gasoline	2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
Gasoline	2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline
Gasoline	2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and 2-tert-butylhydroquinone
Gasoline	2-tert-butylhydroquinone and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and paraffin oil
Gasoline	2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and paraffin oil
Gasoline	6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and 2-tert-butylhydroquinone, 1,2-Propanediol, and paraffin oil

[0033] In one embodiment, the fuel composition comprises a gasoline and an antioxidant mixture comprising 2-tert-butylhydroquinone (TBHQ) and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline (EQ). Such an antioxidant mixture is sold under the trademark SANTOQUIN Q<sup>®</sup> and may be purchased commercially from Novus International, Inc. In another embodiment, the fuel composition comprises a gasoline and an antioxidant mixture comprising 2-tert-butyl-4-hydroxyanisole (BHA) and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene (BHT). In yet another embodiment, the fuel composition comprises a gasoline and an



antioxidant mixture comprising 2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline. In a further embodiment, the fuel composition comprises a gasoline and an antioxidant mixture comprising 2-tert-butylhydroquinone, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, 2-tert-butyl-4-hydroxyanisole, and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene.

[0034] In another embodiment, the fuel composition comprises a gasoline and an antioxidant mixture comprising 2-tert-butylhydroquinone, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, and a paraffin oil. In yet another embodiment, the fuel composition comprises a gasoline and an antioxidant mixture comprising 2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, and a paraffin oil. In a further embodiment, the fuel composition comprises a gasoline and an antioxidant mixture comprising 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, 2-tert-butylhydroquinone, 1,2-Propanediol, and a paraffin oil.

[0035] Those skilled in the art will appreciate that the concentration of antioxidants added to the gasoline can and will vary depending on the desired stability of the fuel. In one embodiment, the fuel composition comprises a gasoline and an antioxidant mixture comprising from about 20 ppm to about 500 ppm of 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, from about 20 ppm to about 500 ppm of a mixture of 2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, and from about 10 to about 60 ppm of 2-tert-butylhydroquinone. In another embodiment, the fuel composition comprises a gasoline and an antioxidant mixture comprising about 400 ppm of 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, about 40 ppm of a mixture of 2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, and about 50 ppm of 2-tert-butylhydroquinone. In yet another embodiment, the fuel composition comprises a gasoline and an antioxidant mixture comprising about 40 ppm of 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, about 40 ppm of a mixture of 2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, and about 50 ppm of 2-tert-butylhydroquinone.

#### **(d) Fuel Composition with Gasoline, Ethanol and at least two Antioxidants**

[0036] In another embodiment, the fuel composition of the invention comprises a gasoline and an ethanol blend in combination with an antioxidant

mixture comprising at least two antioxidants wherein the fuel composition has substantially improved oxidative stability. The fuel composition may comprise from about 15% to about 95% by weight gasoline and from about 5% to about 85% by weight ethanol. In another embodiment, the fuel composition may comprise from about 80% to about 95% by weight gasoline and from about 5% to about 20% by weight ethanol. In an alternative embodiment, the fuel composition may comprise from about 90% to about 95% by weight gasoline and from about 5% to about 10% by weight ethanol. In one embodiment, the fuel composition comprises any of the ethanol described in Part I in combination with a gasoline and an antioxidant mixture comprising at least two antioxidants as described in Part II of the specification above. Exemplary fuel compositions are presented in Table 4 below.

TABLE 4		
Fuel	Ethanol Fuel Raw Material	Antioxidants
Gasoline	Corn	2-tert-butylhydroquinone and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline
Gasoline	Corn	2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
Gasoline	Corn	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline
Gasoline	Corn	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and 2-tert-butylhydroquinone
Gasoline	Corn	2-tert-butylhydroquinone, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and paraffin oil
Gasoline	Corn	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and paraffin oil
Gasoline	Corn	6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, 2-tert-butylhydroquinone, 1,2-Propanediol, and paraffin oil
Gasoline	Plant-derived Cellulose Material	2-tert-butylhydroquinone and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline
Gasoline	Plant-derived Cellulose Material	2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene

TABLE 4		
Fuel	Ethanol Fuel Raw Material	Antioxidants
Gasoline	Plant-derived Cellulose Material	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline
Gasoline	Plant-derived Cellulose Material	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and 2-tert-butylhydroquinone
Gasoline	Plant-derived Cellulose Material	2-tert-butylhydroquinone, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and paraffin oil
Gasoline	Plant-derived Cellulose Material	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and paraffin oil
Gasoline	Plant-derived Cellulose Material	6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, 2-tert-butylhydroquinone, 1,2-Propanediol, and paraffin oil
Gasoline	Sugarcane	2-tert-butylhydroquinone and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline
Gasoline	Sugarcane	2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
Gasoline	Sugarcane	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline
Gasoline	Sugarcane	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and 2-tert-butylhydroquinone
Gasoline	Sugarcane	2-tert-butylhydroquinone, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and paraffin oil
Gasoline	Sugarcane	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and paraffin oil
Gasoline	Sugarcane	6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, 2-tert-butylhydroquinone, 1,2-Propanediol, and paraffin oil
Gasoline	Grain sorghum	2-tert-butylhydroquinone and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline
Gasoline	Grain sorghum	2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
Gasoline	Grain sorghum	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline

TABLE 4		
Fuel	Ethanol Fuel Raw Material	Antioxidants
Gasoline	Grain sorghum	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and 2-tert-butylhydroquinone
Gasoline	Grain sorghum	2-tert-butylhydroquinone, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and paraffin oil
Gasoline	Grain sorghum	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and paraffin oil
Gasoline	Grain sorghum	6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, 2-tert-butylhydroquinone, 1,2-Propanediol, and paraffin oil
Gasoline	Wheat	2-tert-butylhydroquinone and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline
Gasoline	Wheat	2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
Gasoline	Wheat	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline
Gasoline	Wheat	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and 2-tert-butylhydroquinone
Gasoline	Wheat	2-tert-butylhydroquinone, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and paraffin oil
Gasoline	Wheat	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and paraffin oil
Gasoline	Wheat	6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, 2-tert-butylhydroquinone, 1,2-Propanediol, and paraffin oil
Gasoline	Barley	2-tert-butylhydroquinone and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline
Gasoline	Barley	2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
Gasoline	Barley	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline

TABLE 4		
Fuel	Ethanol Fuel Raw Material	Antioxidants
Gasoline	Barley	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and 2-tert-butylhydroquinone
Gasoline	Barley	2-tert-butylhydroquinone, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and paraffin oil
Gasoline	Barley	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and paraffin oil
Gasoline	Barley	6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, 2-tert-butylhydroquinone, 1,2-Propanediol, and paraffin oil
Gasoline	Potatoes	2-tert-butylhydroquinone and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline
Gasoline	Potatoes	2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
Gasoline	Potatoes	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline
Gasoline	Potatoes	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and 2-tert-butylhydroquinone
Gasoline	Potatoes	2-tert-butylhydroquinone, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and paraffin oil
Gasoline	Potatoes	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and paraffin oil
Gasoline	Potatoes	6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, 2-tert-butylhydroquinone, 1,2-Propanediol, and paraffin oil
Gasoline	Biomass	2-tert-butylhydroquinone and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline
Gasoline	Biomass	2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
Gasoline	Biomass	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline

TABLE 4		
Fuel	Ethanol Fuel Raw Material	Antioxidants
Gasoline	Biomass	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and 2-tert-butylhydroquinone
Gasoline	Biomass	2-tert-butylhydroquinone, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and paraffin oil
Gasoline	Biomass	2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and paraffin oil
Gasoline	Biomass	6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline and 2-tert-butylhydroquinone, 1,2-Propanediol, and paraffin oil

[0037] In one embodiment, the fuel composition comprises a gasoline, an ethanol produced from a plant-derived cellulose material, and an antioxidant mixture comprising 2-tert-butylhydroquinone (TBHQ) and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline (EQ). In another embodiment, the fuel composition comprises a gasoline, an ethanol produced from a plant-derived cellulose material, and an antioxidant mixture comprising 2-tert-butyl-4-hydroxyanisole (BHA) and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene (BHT). In yet another embodiment, the fuel composition comprises a gasoline, an ethanol produced from a plant-derived cellulose material, and an antioxidant mixture comprising 2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene and 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline. In a further embodiment, the fuel composition comprises a gasoline, an ethanol produced from a plant-derived cellulose material, and an antioxidant mixture comprising 2-tert-butylhydroquinone, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, 2-tert-butyl-4-hydroxyanisole, and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene.

[0038] In another embodiment, the fuel composition comprises a gasoline, an ethanol produced from a plant-derived cellulose material, and an antioxidant mixture comprising 2-tert-butylhydroquinone, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, and a paraffin oil. In yet another embodiment, the fuel composition comprises a gasoline, an ethanol produced from a plant-derived

cellulose material, and an antioxidant mixture comprising 2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, and a paraffin oil. In a further embodiment, the fuel composition comprises a gasoline, an ethanol produced from a plant-derived cellulose material, and an antioxidant mixture comprising 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, 2-tert-butylhydroquinone, 1,2-Propanediol, and a paraffin oil.

#### Gumming

[0039] Those skilled in the art will appreciate that the concentration of antioxidants added to the gasoline and ethanol blend will generally be the amount needed to achieve an induction period of greater than about 1400 minutes. In one embodiment, the fuel composition comprises a gasoline and ethanol blend, and an antioxidant mixture comprising from about 20 ppm to about 500 ppm of 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, from about 20 ppm to about 500 ppm of a mixture of 2-tert-butyl-4-hydroxyanisole and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, and from about 10 to about 60 ppm of 2-tert-butylhydroquinone.

#### **IV. Additional Agents**

[0040] The fuel compositions of the invention may contain additional agents that enhance one or more characteristics of the fuel. Those skilled in the art will appreciate that the selection of the particular agent may vary considerably depending on the type of fuel used. Suitable additives, for example, may include, but are not limited to, one or more octane improvers, demulsifiers, corrosion inhibitors and/or metal deactivators, cold flow improvers, and the like, as described below.

[0041] Thermal stabilizers may optionally be added to the gasoline composition. Suitable thermal stabilizers known in the art include liquid mixtures of alkyl phenols, including 2-tert-butylphenol, 2,6-di-tert-butylphenol, 2-tert-butyl-4-n-butylphenol, 2,4,6-tri-tert-butylphenol, and 2,6-di-tert-butyl-4-n-butylphenol. Other commercially available hindered phenolic antioxidants that also exhibit a thermal stability effect include 2,6-di-t-butyl-4-methylphenol; 2,6-di-t-butylphenol; 2,2'-methylene-bis(6-t-butyl-4-methylphenol); n-octadecyl 3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate; 1,1,3-tris(3-t-butyl-6-methyl-4hydroxyphenyl) butane;

pentaerythrityl tetrakis[3-(3,5-di-t-butyl-4-hydroxyphenyl) propionate]; di-n-octadecyl(3,5-di-t-butyl-4-hydroxybenzyl)phosphonate; 2,4,6-tris(3,5-di-t-butyl-4-hydroxybenzyl) mesitylene; and tris(3,5-di-t-butyl-4-hydroxybenzyl)isocyanurate. Additional suitable thermal stabilizers include: pentaerythritol co-esters derived from pentaerythritol, (3-alkyl-4-hydroxyphenyl)-alkanoic acids and alkylthioalkanoic acids or lower alkyl esters of such acids which are useful as stabilizers of organic material normally susceptible to oxidative and/or thermal deterioration.

[0042] Certain lubricating fluid base stocks are known in the art to exhibit high thermal stability and as such, may be beneficial in certain embodiments of the invention. Suitable base stocks include polyalphaolefins, dibasic acid esters, polyol esters, alkylated aromatics, polyalkylene glycols, and phosphate esters.

[0043] A variety of polyalphaolefins may be utilized in the fuel composition of the invention. Polyalphaolefins are hydrocarbon polymers that contain no sulfur, phosphorus, or metals.

[0044] In another embodiment, the fuel composition may optionally include a carburetor detergent. Carburetor deposits may form in the throttle body and plate, idle air circuit, and in the metering orifices and jets. These deposits are a combination of contaminants from dust and engine exhaust, held together by gums formed from unsaturated hydrocarbons in the fuel. They can alter the air/fuel ratio, cause rough idling, increased fuel consumption, and increased exhaust emissions. Carburetor detergents appropriate for use in the invention typically prevent deposits from forming and remove deposits already formed.

[0045] In yet another embodiment, the fuel composition may optionally include a fuel injector detergent. Fuel injectors are very sensitive to deposits that can reduce fuel flow and alter the injector spray pattern. These deposits can make vehicles difficult to start, cause severe drive ability problems, and increase fuel consumption and exhaust emissions. Suitable detergents include amine detergents and polymeric dispersants.

[0046] In another embodiment, the fuel composition may optionally include an agent to minimize combustion chamber deposits. Combustion chamber deposits can cause an increase in the octane number requirement for vehicles as they accumulate miles. These deposits accumulate in the end-gas zone and injection port area. Suitable agents that minimize combustion chamber deposits include



polyetheramine and other proprietary additives are known to reduce the magnitude of combustion chamber deposits.

[0047] The gasoline fuel compositions of various embodiments advantageously may contain one or more drive ability additives, such as anti-knock, anti-run-on, anti-pre-ignition, and anti-misfire additives that directly affect the combustion process. Anti-knock additives include lead alkyls that are no longer used in the United States. These and other metallic anti-knock additives are typically used at dosages of roughly 0.2 g metal/liter of fuel (or about 0.1 wt % or 1000 ppm). A typical octane number enhancement at this dosage level is 3 units for both Research Octane Number (RON) and Motor Octane Number (MON). Several organic compounds are also known to have anti-knock activity. These include aromatic amines, alcohols, and ethers that can be employed at dosages in the 1000 ppm range. These additives work by transferring hydrogen to quench reactive radicals. Oxygenates such as methanol and MTBE also increase octane number but these are used at such high dosages that they are not really additives but blend components. Pre-ignition is generally caused by the presence of combustion chamber deposits and is treated using combustion chamber detergents and by raising octane number.

[0048] The fuel composition may include a variety of demulsifiers. Demulsifiers are molecules that aid the separation of oil from water usually at very low concentrations. They prevent formation of a water and oil mixture. Several demulsifiers are available for use in the fuel formulations of various embodiments, including, for example, organic sulfonates, polyoxyalkylene glycols, oxyalkylated phenolic resins, and like materials. Exemplary formulations include alkylaryl sulfonates, polyoxyalkylene glycols and oxyalkylated alkylphenolic resins, such as are available commercially from Baker Petrolite Corporation of Sugar Land, Tex. as TOLAD®.

[0049] Several corrosion inhibitors are suitable for use in the fuel formulations of various embodiments. Suitable corrosion inhibitors include dimer and trimer acids, such as are produced from tall oil fatty acids, oleic acid, linoleic acid, or the like. Other suitable corrosion inhibitors are the alkenyl succinic acid and alkenyl succinic anhydride corrosion inhibitors such as, for example, tetrapropenylsuccinic acid, tetrapropenylsuccinic anhydride, tetradecenylsuccinic

acid, tetradecenylsuccinic anhydride, hexadecenylsuccinic acid, hexadecenylsuccinic anhydride, and the like. Also useful are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols.

[0050] If desired, the fuel compositions may contain a metal deactivator of the type having the ability to form complexes with heavy metals such as copper and the like. Typically, the metal deactivators used are gasoline soluble N,N'-disalicylidene-1,2-alkanediamines or N,N'-disalicylidene-1,2-cycloalkanediamines, or mixtures thereof. Examples include N,N'-disalicylidene-1,2-ethanediamine, N,N'-disalicylidene-1,2-propanediamine, N,N'-disalicylidene-1,2-cyclo-hex- anediamine, and N,N"-disalicylidene-N'-methyl-dipropylene-triamine.

[0051] The fuel composition may include a variety of oxygenates. Oxygenates are added to gasoline to improve octane number and to reduce emissions of CO. These include various alcohols and ethers that are typically blended with gasoline to produce an oxygen content typically of up to about 2 weight percent, although higher concentrations may be desirable in certain embodiments. Suitable examples of oxygenates include methanol, ethanol, methyl tertiary butyl ether (MTBE), ethyl tertiary butyl ether (ETBE), diisopropyl ether (DIPE), and tertiary amyl methyl ether (TAME).

[0052] The amount of additive that may be included in the various fuel compositions of the invention can and will vary. The amount will typically be the amount that is sufficient to impart the desired functional property to the fuel composition.

## ***V. Methods for Improving Oxidative Stability and Reducing Gum Formation***

[0053] As demonstrated in the examples, the fuel compositions of the invention typically have increased oxidative stability. In addition to having increased oxidative stability, depending on the embodiment, the fuel compositions may also have reduced gumming. The method of increasing the oxidative stability of a fuel composition and/or reducing gumming typically comprises contacting a gasoline with an antioxidant mixture that increases the oxidative stability of the fuel. In another embodiment, the method of increasing the oxidative stability of a fuel composition

and/or reducing gumming typically comprises contacting a gasoline and ethanol blend with an antioxidant mixture that increases the oxidative stability of the fuel.

[0054] Methods for determining oxidative stability of a fuel composition and/or a reduction in gum formation may be determined by methods generally known in the art, such as, for example, by the ASTM test D525 for Oxidation Stability. Potential gum is indicative of oxidation, and may be determined by the ASTM test D525 for Oxidation Stability as described more fully in the Examples. For automotive gasoline, the potential gum may be expressed as the "induction period" (sometimes called the breakdown time). This is a measure of the time (in minutes) elapsed during the accelerated test until the fuel absorbs oxygen rapidly. The ASTM test D525 for Oxidation Stability of Gasoline (Induction Period Method) utilizes accelerated oxidation conditions to determine the oxidation stability of gasoline. This method may be utilized by a skilled artisan to formulate blends of antioxidants having a suitable concentration of each ingredient in order for the antioxidant blend to impart the desired oxidative stability for the fuel of the invention. In one embodiment, the fuel compositions of the present invention have an induction time greater than 450 minutes, greater than about 500 minutes, greater than about 550 minutes, greater than about 600 minutes, greater than about 650 minutes, greater than about 700 minutes, greater than about 750 minutes, greater than about 800 minutes, greater than about 850 minutes, greater than about 900 minutes, greater than about 950 minutes, greater than about 1000 minutes, greater than about 1050 minutes, greater than about 1100 minutes, greater than about 1150 minutes, greater than about 1200 minutes, greater than about 1250 minutes, greater than about 1300 minutes, greater than about 1350 minutes, greater than about 1400 minutes, or greater than about 1450 minutes.

## **DEFINITIONS**

[0055] To facilitate understanding of the invention, a number of terms and abbreviations as used herein are defined below:

[0056] The term "Induction time" denotes the resistance of the fuel to oxidation.

[0057] The term "Oxidative Stability" refers to the ability to decrease the rate of fuel oxidation.

[0058] The term "PPM" stands for parts per million.

[0059] As various changes could be made in the above fuel compositions, products and methods without departing from the scope of the invention, it is intended that all matter contained in the above description shall be interpreted as illustrative and not in a limiting sense.

### **EXAMPLES**

[0060] The following examples illustrate various iterations of fuel compositions having improved oxidative stability.

#### ***Example 1. Improved Oxidative Stability of Fuel Compositions Comprising Ethoxyquin.***

[0061] The ability of the antioxidant 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, also known as ethoxyquin, to stabilize gasoline mixtures was tested. Ethoxyquin was added at concentrations of 0.01% (100 ppm) or 0.005% (50 ppm) to gasoline compositions comprising from 0% to 85% of ethanol. The base fuel used for blending was an ethanol blending Reformulated gasoline Blendstock for Oxygen Blending (RBOB). The fuel was obtained from the terminal prior to the addition of any detergent additives or oxygenates. The fuel was filtered through Alumina to remove any antioxidant additives that would be present from the refinery blendstock fuels. (See Examples 2 and 3 for additional information about the base fuel used in this study.)

[0062] The oxidative stability of each of the formulations (see Table 1) was tested using the ASTM D 525 Test Method for Oxidation Stability of Gasoline (Induction Period Method). Analyses were performed according to the listed ASTM test procedures with no modifications or deviations. Briefly, a sample of gasoline was placed in a glass sample container in a pressure vessel and oxygen was introduced to a pressure of about 100 psi. The charged pressure vessel was placed in a 100°C (212°F) bath and the pressure was continuously monitored for 24 hours (1440 minutes). The break point of the fuel was determined when a specified drop in pressure in 15 minutes was observed. The number of minutes required to reach this point was the induction period.

[0063] Table 1 presents the induction periods, maximum and minimum pressures, and indicates whether or not a break point was observed. Ethoxyquin (ETX) increased the induction period of fuels comprising 0%, 10%, and 20% ethanol about three-fold. Fuels comprising 40% or more ethanol were stable with and without the antioxidant. Figures 1-3 present pressure versus time plots in the absence or presence of ethoxyquin of the different fuel compositions. The plots clearly indicate the breaking points or lack of breaking points in the various formulations.

Table 1. ASTM D 525 Test Results.

Run #	Sample Composition (%)			Induction Period (min)	Break	Max Pressure (psi)	Min Pressure (psi)
	Fuel	EtOH	ETX				
1	100	0	0	238	YES	148.9	54.5
2	99.99	0	0.01	718	YES	150.5	54.4
3	89.99	10	0.01	894	YES	163.7	68.3
4	90	10	0	315	YES	162.9	64.4
5	79.99	20	0.01	>1440	No Break	172.7	80.8
6	80	20	0	582	YES	168.0	68.3
7	59.99	40	0.01	>1440	No Break	168.8	114.7
8	60	40	0	>1440	No Break	166.9	66.4
9	39.99	60	0.01	>1440	No Break	166.1	164.4
10	40	60	0	>1440	No Break	166.0	81.8
11	14.99	85	0.01	>1440	No Break	158.3	157.4
12	15	85	0	>1440	No Break	161.1	150.2
13	14.995	85	0.005	>1440	No Break	158.5	157.0
14	39.995	60	0.005	>1440	No Break	165.0	1337
15	79.995	20	0.005	>1440	No Break	169.0	68.2
16	89.995	10	0.005	563	YES	170.4	69.3

**Example 2. Distillation Profile of Base Fuel.**

[0064] The base fuel used in Example 1 was characterized by determining its distillation profile. This was determined using the ASTM D 86 Standard Test Method for Distillation of Petroleum Products at Atmospheric Pressure. For this, a sample was placed in a round bottom flask and heated at a rate specified for samples with its vapor pressure characteristics. Temperatures (°F) were recorded when the first drop was collected (initial boiling point; IBP), at recovered volumes representing 5% to 95% of the initial volume, and at the end of the test (final boiling point; FBP).

[0065] The distillation profile is presented in Table 2, as well as the percentages of recovery, residue, and loss.

Table 2. ASTM D 86 Distillation Profile of Fuel.

Measured	Unit	Value
IBP	°F	83.7
5%	°F	100.3
10%	°F	114.7
15%	°F	124.5
20%	°F	134.2
30%	°F	154.8
40%	°F	177.4
50%	°F	201.5
60%	°F	227.9
70%	°F	258.6
80%	°F	299.0
90%	°F	349.5
95%	°F	383.6
FBP	°F	421.9
Recovery	%	96.5
Residue	%	0.9
Loss	%	2.6

**Example 3. Composition of Base Fuel.**

[0066] The base fuel used in Example 1 was characterized by determining its composition of hydrocarbons. This analysis was performed using the ASTM D 6729 Test Method for Determination of Individual Components in Spark Ignition Engine Fuels by Capillary High-Resolution Gas Chromatography. The method uses a 100 meter capillary column and flame ionization detector. A total of 385 compounds were identified. The compounds are summarized by group in Table 3. The compounds are summarized by number of carbons in Table 4, and composite in Table 5.

Table 3. Base Fuel Composition: Summary by Group.

Group	% Weight	% Volume	% Mole
Paraffin	12.957	14.844	16.232
I-Paraffins	35.824	39.009	36.675
Aromatics	29.550	24.535	24.978
Mono-Aromatics	26.270	22.016	22.559
Naphthalenes	1.400	1.007	1.003
Naphtheno/Olefino-Benz	1.247	1.025	0.920
Indenes	0.520	0.394	0.429
Naphthenes	6.501	6.201	6.239
Mono-Naphthenes	6.046	5.776	5.894
Di/Bicyclo-Naphthenes	0.051	0.046	0.032
Olefins	10.021	10.702	12.018
n-Olefins	3.711	4.066	4.658
Iso-Olefins	4.528	4.877	5.410
Naphtheno-Olefins	0.692	0.649	0.863
Di-Olefins	0.455	0.462	0.497
Oxygenates	0.131	0.129	0.148

Table 4. Base Fuel Composition: Summary by Carbon.

Carbon #	% Weight	% Volume	% Mole
C4	4.343	5.480	7.299
C5	14.084	16.206	19.178
C6	14.295	15.409	16.349
C7	19.729	19.798	19.652
C8	17.146	16.333	15.141
C9	11.800	10.611	9.369
C10	7.890	6.713	5.747
C11	3.242	2.735	2.120
C12	2.083	1.775	1.238
C13	0.371	0.359	0.196

Table 5. Base Fuel Composition: Composite by Carbon.

Group	Carbon #	% Weight	% Volume	% Mole
Paraffin	C4	3.601	4.549	6.039
	C5	2.888	3.372	3.901
	C6	2.889	3.204	3.268
	C7	1.729	1.849	1.682
	C8	0.700	0.728	0.597
	C9	0.348	0.355	0.265
	C10	0.232	0.233	0.159
	C11	0.164	0.162	0.103
	C12	0.121	0.118	0.069
	C13	0.283	0.274	0.150
I-Paraffins	C4	0.396	0.520	0.664
	C5	6.697	7.905	9.047
	C6	7.629	8.485	8.628



	C7	8.657	9.319	8.421
	C8	7.634	7.961	6.514
	C9	2.539	2.578	1.929
	C10	1.177	1.173	0.806
	C11	0.810	0.792	0.506
	C12	0.198	0.192	0.113
	C13	0.088	0.085	0.047
Aromatics	C12	0.113	0.093	0.068
Mono-Aromatics	C6	0.715	0.595	0.892
	C7	4.284	3.613	4.532
	C8	7.001	5.899	6.428
	C9	7.429	6.233	6.025
	C10	3.866	3.238	2.807
	C11	1.502	1.227	0.991
	C12	1.474	1.211	0.885
Naphthalenes	C10	0.662	0.478	0.500
	C11	0.738	0.529	0.502
Naphtheno/Olefino-Benzs	C10	1.247	1.025	0.920
Indenes	C10	0.520	0.394	0.429
Naphthenes	C8	0.054	0.050	0.047
	C9	0.322	0.302	0.249
	C11	0.028	0.026	0.018
Mono-Naphthenes	C5	0.434	0.426	0.604
	C6	0.580	0.544	0.671
	C7	2.954	2.848	2.933
	C8	1.264	1.200	1.098

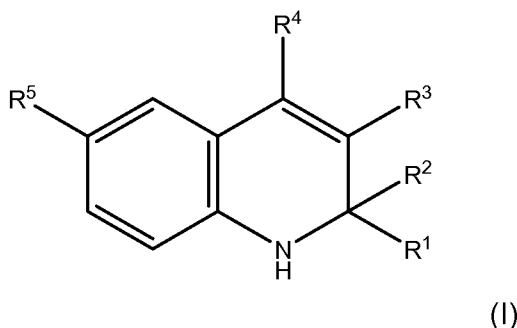
	C9	0.559	0.526	0.432
	C10	0.079	0.071	0.055
	C12	0.176	0.161	0.102
Di/Bicyclo-Naphthenes	C10	0.051	0.046	0.032
Olefins	C4	0.000	0.000	0.000
	C6	0.046	0.049	0.053
	C7	0.240	0.250	0.231
	C8	0.170	0.169	0.163
	C9	0.179	0.181	0.142
n-Olefins	C4	0.334	0.400	0.580
	C5	1.650	1.860	2.293
	C6	0.881	0.942	1.021
	C7	0.432	0.448	0.429
	C8	0.182	0.185	0.158
	C9	0.216	0.214	0.167
	C10	0.017	0.017	0.012
Iso-Olefins	C5	2.015	2.246	2.800
	C6	1.048	1.115	1.214
	C7	1.217	1.255	1.208
	C9	0.208	0.221	0.161
	C10	0.040	0.040	0.028
Naphtheno-Olefins	C5	0.180	0.171	0.258
	C6	0.496	0.463	0.589
	C7	0.016	0.015	0.016
Di-Olefins	C5	0.101	0.109	0.145
	C6	0.011	0.012	0.013
	C7	0.200	0.201	0.201

Oxygenates	C8	0.143	0.141	0.138
	C4	0.012	0.011	0.016
	C5	0.119	0.117	0.132

**CLAIMS**

What is Claimed is:

1. A fuel composition, the composition comprising:
  - (a) A gasoline;
  - (b) An ethanol; and
  - (c) An antioxidant comprising Formula (I):



wherein:

$R^1$ ,  $R^2$ ,  $R^3$  and  $R^4$  are independently selected from the group consisting of hydrogen and an alkyl group having from 1 to about 6 carbons;

$R^5$  is an alkoxy group having from 1 to about 12 carbons.

2. The fuel composition of claim 1, comprising at least one additional antioxidant selected from the group consisting of butylated hydroxyanisole; butylated hydroxytoluene; octyl gallate; dodecyl gallate; 3,4,5-trihydroxybenzoic acid n-propyl ester; 1,2,3-trihydroxybenzene; methyl linoleate; methyl oleate; methyl stearate; 2,2,6,6-tetramethylpiperidinoxy; 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl; dimethyl-p-phenylaminophenoxysilane; di-p-anisylazoxides; p-hydroxydiphenylamine; ascorbyl palmitate; butylated hydroxyanisole; butylated hydroxytoluene; phenyl-alpha-naphthylamine; hydroquinone; 2-tert-butylhydroquinone; 3-tertiarybutyl-4-hydroxyanisole; 2,6-di-tert-butyl-4-hydroxymethylphenol; 2,6-di-tert-butyl-4-methylphenol; t-tert-butyl-4-methylphenol; 2-ter-butyl-4-methoxyphenol; polyphosphates; trihydroxy butyrophenone; and anoxomer.

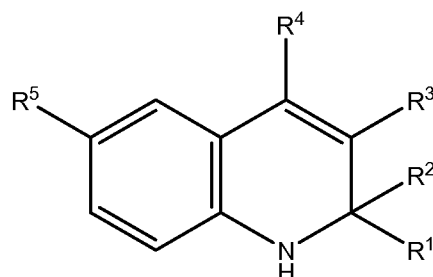
3. The fuel composition of claim 1, comprising at least one additional antioxidant selected from the group consisting of 2-tert-butylhydroquinone; 3,4,5-trihydroxybenzoic acid n-propyl ester; mono tertiary butyl hydroquinone; di-tert-butyl hydroquinone; 1,2,3-trihydroxybenzene; 2-tert-butyl-4-hydroxyanisole; t-tert-butyl-4-methylphenol; and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene.
4. The fuel composition of claim 1, wherein the antioxidant is 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline.
5. The fuel composition of claim 4, wherein the fuel contains from about 20 ppm to about 1500 ppm 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline.
6. The fuel composition of claim 4, wherein the fuel contains from about 50 ppm to about 500 ppm 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline.
7. The fuel composition of claim 4, further comprising 2-tert-butylhydroquinone.
8. The fuel composition of claim 4, further comprising 2-tert-butyl-4-hydroxyanisole; and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
9. The fuel composition of claim 4, further comprising 2-tert-butylhydroquinone, and a paraffin oil.
10. The fuel composition of claim 4, further comprising 2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, and a paraffin oil.
11. The fuel composition of claim 1, wherein the fuel comprises from about 60% to about 99% by weight gasoline and from about 1% to about 40% by weight ethanol.

12. The fuel composition of claim 1, wherein the fuel comprises from about 80% to about 90% by weight gasoline and from about 10% to about 20% by weight ethanol.
13. The fuel composition of claim 1, wherein the fuel has substantially improved oxidative stability.
14. The fuel composition of claim 1, wherein the fuel has an induction time of greater about than 1400 minutes.
15. The fuel composition of claim 1, wherein the fuel has substantially reduced gumming.
16. The fuel composition of claim 1, further comprising an additive selected from the group comprising of octane improvers, drive ability additives, metal deactivators, corrosion inhibitors, thermal stabilizers, detergents, and demulsifiers.
17. The fuel composition of claim 1, further comprising a solvent selected from the group consisting of a polar solvent and a non polar solvent.
18. A fuel composition, the composition comprising:
  - (a) A gasoline in an amount ranging from about 60% to about 99% by weight of the composition;
  - (b) An ethanol in an amount ranging from about 1% to about 40% by weight of the composition; and
  - (c) 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline in an amount ranging from about 20 to about 1500 ppm.
19. The fuel composition of claim 18, wherein the composition comprises about 80% to about 90% by weight gasoline; from about 10% to about 20% by weight ethanol; and from about 50 ppm to about 500 ppm 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline.

20. The fuel composition of claim 18, comprising at least one additional antioxidant selected from the group consisting of butylated hydroxyanisole; butylated hydroxytoluene; octyl gallate; dodecyl gallate; 3,4,5-trihydroxybenzoic acid n-propyl ester; 1,2,3-trihydroxybenzene; methyl linoleate; methyl oleate; methyl stearate; 2,2,6,6-tetramethylpiperidinoxy; 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl; dimethyl-p-phenylaminophenoxysilane; di-p-anisylazoxides; p-hydroxydiphenylamine; ascorbyl palmitate; butylated hydroxyanisole; butylated hydroxytoluene; phenyl-alpha-naphthylamine; hydroquinone; 2-tert-butylhydroquinone; 3-tertiarybutyl-4-hydroxyanisole; 2,6-di-tert-butyl-4-hydroxymethylphenol; 2-6-di-tert-butyl-4-methylphenol; t-tert-butyl-4-methylphenol; 2-ter-butyl-4-methoxyphenol; polyphosphates; trihydroxy butyrophenone; and anoxomer.
21. The fuel composition of claim 18, comprising at least one additional antioxidant selected from the group consisting of 2-tert-butylhydroquinone; 3,4,5-trihydroxybenzoic acid n-propyl ester; mono tertiary butyl hydroquinone; di-tert-butyl hydroquinone; 1,2,3-trihydroxybenzene, 2-tert-butyl-4-hydroxyanisole; t-tert-butyl-4-methylphenol; and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene.
22. The fuel composition of claim 18, further comprising 2-tert-butylhydroquinone.
23. The fuel composition of claim 18, further comprising 2-tert-butyl-4-hydroxyanisole; and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
24. The fuel composition of claim 18, further comprising 2-tert-butylhydroquinone, and a paraffin oil.

25. The fuel composition of claim 18, further comprising 2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, and a paraffin oil.
26. The fuel composition of claim 18, wherein the fuel has an improved oxidative stability.
27. The fuel composition of claim 18, wherein the fuel has an induction time of greater than 1400 minutes.
28. The fuel composition of claim 18, wherein the fuel has substantially reduced gumming.
29. The fuel composition of claim 18, wherein the ethanol is produced from a source selected from the group consisting of corn, plant-derived cellulose material, sugarcane, sugar beet, grain sorghum, sugar cane, sugar beet, wheat, barley, potatoes, and biomass.
30. The fuel composition of claim 18, further comprising an additive selected from the group comprising of octane improvers, drive ability additives, metal deactivators, corrosion inhibitors, thermal stabilizers, detergents, and demulsifiers.
31. The fuel composition of claim 18, further a solvent selected from the group consisting of a polar solvent and a non polar solvent.
32. A method for increasing the oxidative stability of a fuel composition, the fuel composition comprising gasoline and ethanol, the method comprising contacting the fuel composition with an antioxidant comprising Formula (I):





(I)

wherein:

R<sup>1</sup>, R<sup>2</sup>, R<sup>3</sup> and R<sup>4</sup> are independently selected from the group consisting of hydrogen and an alkyl group having from 1 to about 6 carbons;

R<sup>5</sup> is an alkoxy group having from 1 to about 12 carbons.

33. The method of claim 32, comprising at least one additional antioxidant selected from the group consisting of butylated hydroxyanisole; butylated hydroxytoluene; octyl gallate; dodecyl gallate; 3,4,5-trihydroxybenzoic acid n-propyl ester; 1,2,3-trihydroxybenzene; methyl linoleate; methyl oleate; methyl stearate; 2,2,6,6-tetramethylpiperidinoxy; 2,2,6,6-tetramethyl-4-hydroxypiperidine-1-oxyl; dimethyl-p-phenylaminophenoxysilane; di-p-anisylazoxides; p-hydroxydiphenylamine; ascorbyl palmitate; butylated hydroxyanisole; butylated hydroxytoluene; phenyl-alpha-naphthylamine; hydroquinone; 2-tert-butylhydroquinone; 3-tertiarybutyl-4-hydroxyanisole; 2,6-di-tert-butyl-4-hydroxymethylphenol; 2,6-di-tert-butyl-4-methylphenol; t-tert-butyl-4-methylphenol; 2-ter-butyl-4-methoxyphenol; polyphosphates; trihydroxy butyrophenone; and anoxomer.
34. The method of claim 32, comprising at least one additional antioxidant selected from the group consisting of 2-tert-butylhydroquinone; 3,4,5-trihydroxybenzoic acid n-propyl ester; mono tertiary butyl hydroquinone; di-tert-butyl hydroquinone; 1,2,3-trihydroxybenzene, 2-tert-butyl-4-hydroxyanisole, t-tert-butyl-4-methylphenol; and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene.

35. The method of claim 32, wherein the antioxidant is 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline.
36. The method of claim 35, wherein the fuel contains from about 20 ppm to about 1500 ppm 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline.
37. The method of claim 35, wherein the fuel contains from about 50 ppm to about 500 ppm 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline.
38. The method of claim 35, further comprising 2-tert-butylhydroquinone.
39. The method of claim 35, further comprising 2-tert-butyl-4-hydroxyanisole; and 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene
40. The method of claim 35, further comprising 2-tert-butylhydroquinone, and a paraffin oil.
41. The method of claim 35, further comprising 2-tert-butyl-4-hydroxyanisole, 2,6-Di-tert-Butyl-1-Hydroxy-4-Methylbenzene, and a paraffin oil.
42. The method of claim 32, wherein the fuel comprises from about 60% to about 99% by weight gasoline and from about 1% to about 40% by weight ethanol.
43. The method of claim 32, wherein the fuel comprises from about 80% to about 90% by weight gasoline and from about 10% to about 20% by weight ethanol.
44. The method of claim 32, wherein the fuel has an induction time of greater about than 1400 minutes.

45. The method of claim 32, wherein the ethanol is produced from a source selected from the group consisting of corn, plant-derived cellulose material, sugarcane, sugar beet, grain sorghum, sugar cane, sugar beet, wheat, barley, potatoes, and biomass.

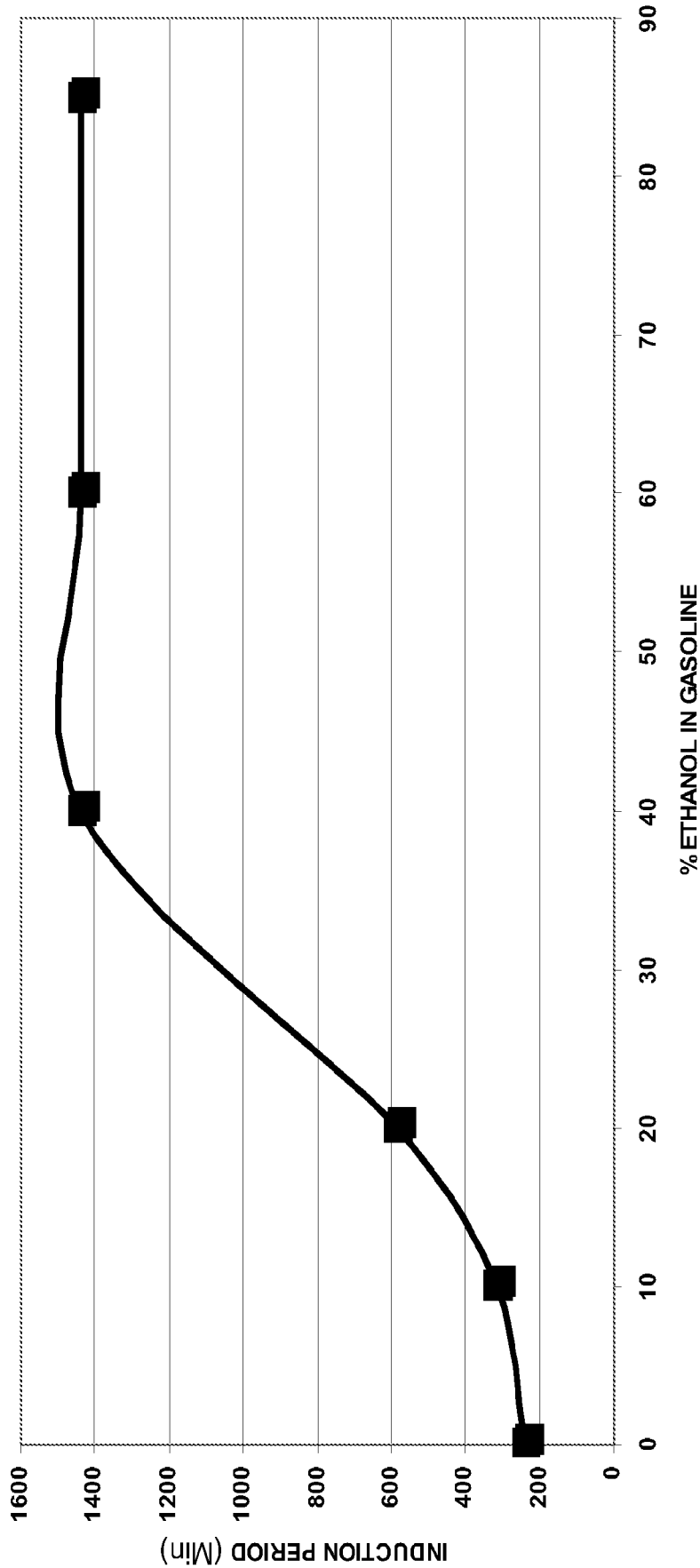


FIG. 1

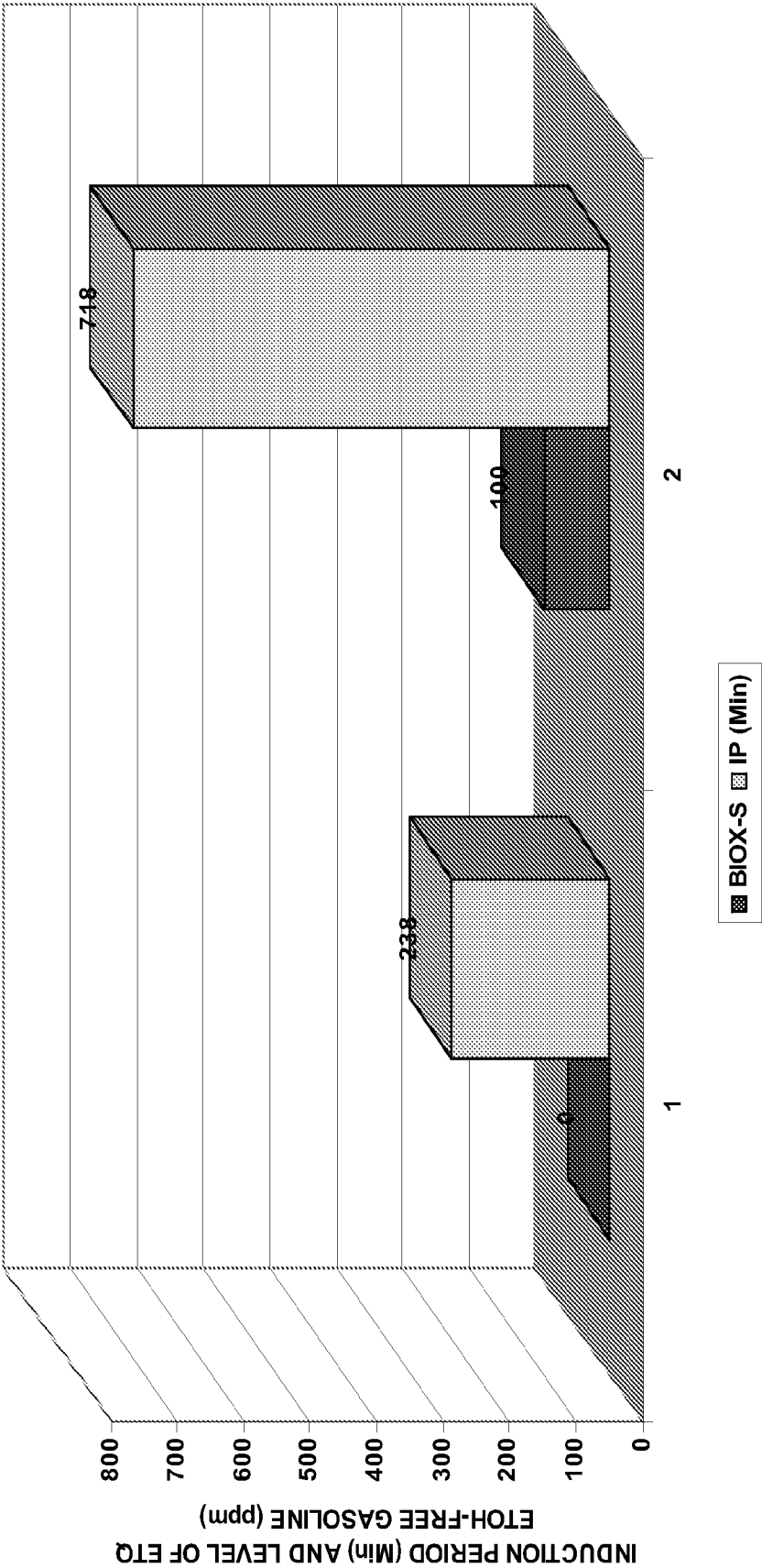


FIG. 2

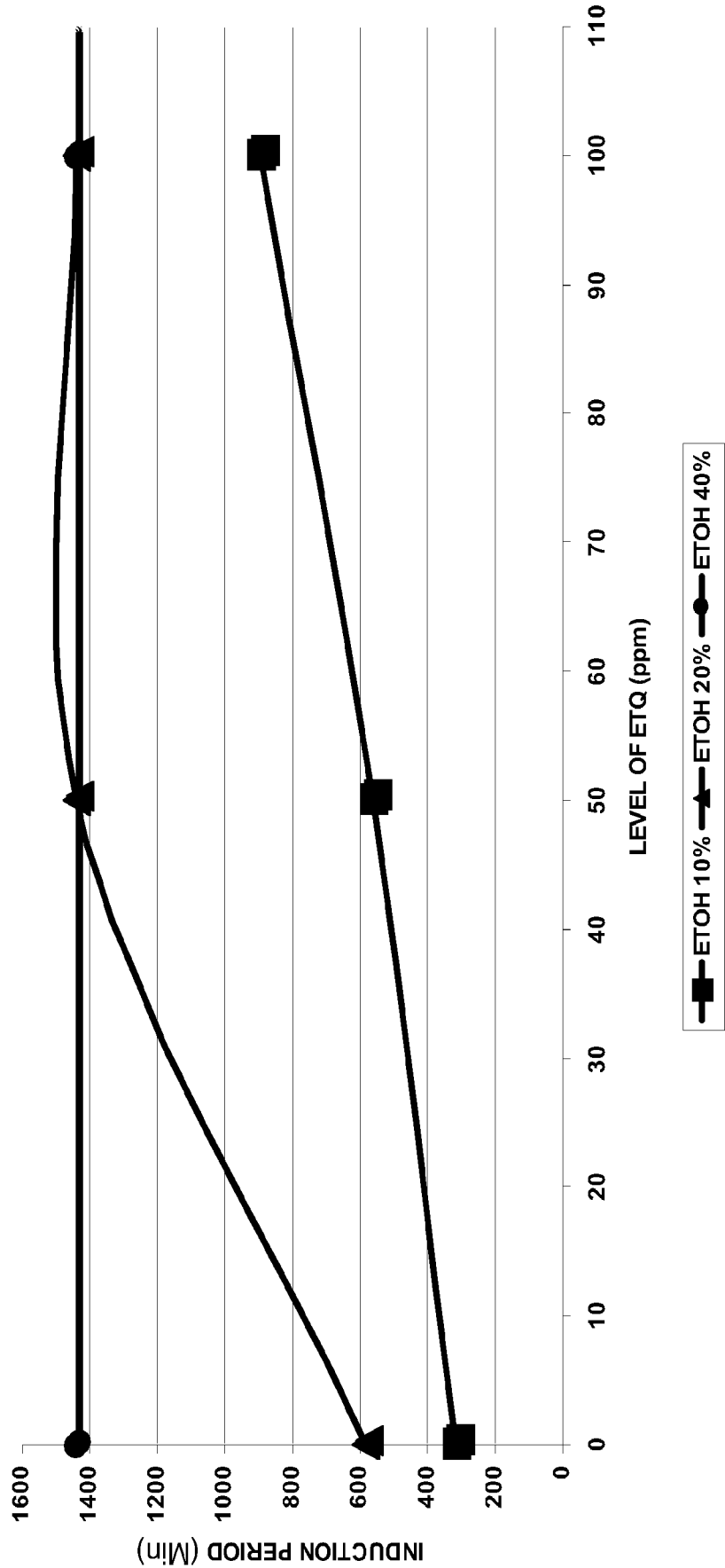


FIG. 3