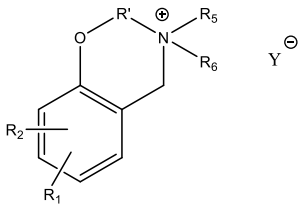
quaternized detergents are typically derived from PIBSI compounds that have pendant tertiary amine sites that can be alkylated, or quaternized, by hydrocarbyl epoxides, such as propylene oxide.

[0005] While providing improved detergency compared to prior detergents, these quaternary ammonium compounds and their methods of alkylation, however, still have several shortcomings. For instance, quaternary ammonium salts detergents often require the use of flammable and undesired epoxides, such as ethylene oxide propylene oxide, and/or require the use of specialized and expensive pressure vessels for their production. Such oxides, however, are often undesired due to their handling difficulties. In other instances, the alkoxylation step requires a carboxylic acid as proton donor. The resulting carboxylate may lead to deposit formation and other issues related to carboxylate salts being present in the additive and fuel. In other instances, the polyisobutenyl succinamide and/or ester intermediates tend to be viscous and/or difficult to handle during the manufacturing process. The reaction products often contain varying amounts of polyisobutenyl succinimides rendering it difficult to charge a correct amount of epoxide and/or acid to the reaction mixture. In other instances, quaternary ammonium compounds may be formed through alkylation using dialkyl carbonates. However, the carbonate anion may be susceptible to precipitation and drop out of certain types of fuels or fuel additive packages. Thus, prior quaternary ammonium compounds may have various shortcomings in their manufacture and/or application.

SUMMARY

[0006] As described herein is a quaternary ammonium salt fuel additive comprising the structure of Formula Ib. In examples, the additive of Formula Ib has the following structure:

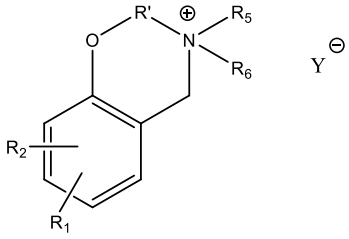


(Formula Ib)

wherein R_1 is a hydrocarbyl radical, wherein a molecular weight of the hydrocarbyl is about 200 to about 5,000; R_2 is hydrogen or a C_1-C_6 alkyl group; R' is a C_1 to C_4 alkyl linker; R_5 is

C_1-C_6 alkyl or, together with $Y^{\ominus}$, forms a C_1-C_6 alkyl substituted –C(O)$O^{\ominus}$; R_6 is C_1-C_6 alkyl; and $Y^{\ominus}$ is an anionic group having a structure $R_8C(O)O^{\ominus}$ wherein R_8 is one of (i) together with R_5 a C_1-C_6 alkyl group or (ii) a C_1-C_6 alkyl, an aryl, a C_1-C_4 alkylene–C(O)O-R_2 or a –C(O)O-R_2 group.

[0006a] In a first aspect of the present disclosure, there is provided a quaternary ammonium salt fuel additive comprising the structure of Formula Ib



(Formula Ib)

wherein

R_1 is a hydrocarbyl radical, wherein a molecular weight of the hydrocarbyl is 200 to 5,000;

R_2 is hydrogen or a C_1-C_6 alkyl group;

R' is a C_1 to C_4 alkyl linker;

R_5 is C_1-C_6 alkyl or, together with $Y^{\ominus}$, forms a C_1-C_6 alkyl substituted –C(O)$O^{\ominus}$;

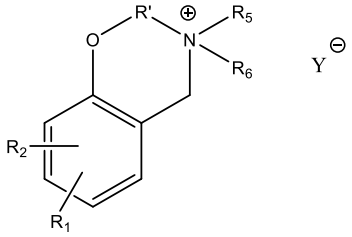
R_6 is C_1-C_6 alkyl; and

$Y^{\ominus}$ is an anionic group having a structure $R_8C(O)O^{\ominus}$ wherein R_8 is one of (i) together with R_5 a C_1-C_6 alkyl group or (ii) a C_1-C_6 alkyl, an aryl, a C_1-C_4 alkylene–C(O)O-R_2 or a –C(O)O-R_2 group.

[0007] In other approaches or examples, the quaternary ammonium salt fuel additive of the previous paragraph may be combined with other features, examples, or approaches in any combination. Such examples may include one or more of the following: wherein R_1 is a hydrocarbyl radical derived from polyisobutylene polymer or oligomer, which has a number average molecular weight of 500 to 1500, R_2 is hydrogen or a methyl group, and R' is a -CH_2- group; and/or wherein R_5 is C_1-C_6 alkyl and wherein $Y^{\ominus}$ is the anionic group having the structure $R_8C(O)O^{\ominus}$ with R_8 being the C_1-C_6 alkyl, the aryl, the C_1-C_4 alkylene–C(O)O-R_2 or the –C(O)O-R_2 group; and/or wherein R_5 is C_1-C_6 alkyl and wherein $Y^{\ominus}$ is the anionic group having the structure $R_8C(O)O^{\ominus}$ with R_8 being the –C(O)O-R_2 group; and/or wherein the quaternary ammonium salt fuel additive is derived from (i) a Mannich reaction product or derivative thereof having at least one tertiary amino group and prepared from a hydrocarbyl-substituted phenol, cresol, or derivative thereof, an aldehyde, and a hydrocarbyl amine providing the tertiary amino group and reacted with (ii) a quaternizing agent selected from the group consisting of a carboxylic or polycarboxylic acid, ester, amide, or salt thereof or halogen substituted derivative thereof; and/or wherein the hydrocarbyl amine is a C_1 to C_4 alkyl amine; and/or wherein the quaternizing agent is a diester of a dicarboxylic acid; and/or wherein the quaternizing agent is a diester of oxalic acid, phthalic acid, maleic acid, or malonic acid, or combinations thereof; and/or wherein the quaternizing agent is a halogen substituted derivative of a carboxylic acid; and/or wherein the halogen substituted derivative of a carboxylic acid is a mono-, di-, or tri- chloro- bromo-, fluoro-, or iodo-carboxylic acid, ester, amide, or salt thereof selected from the group consisting of halogen-substituted acetic acid, propanoic acid, butanoic acid, isopropanoic acid, isobutanoic acid, *tert*-butanoic acid, pentanoic acid, heptanoic acid, octanoic acid, halo-methyl benzoic acid, and isomers, esters, amides, and salts thereof; and/or wherein the quaternary ammonium salt fuel additive is an internal salt substantially devoid of free anion species.

[0008] As described herein is a fuel composition comprising a major amount of fuel and a minor amount of a quaternary ammonium salt having the structure of

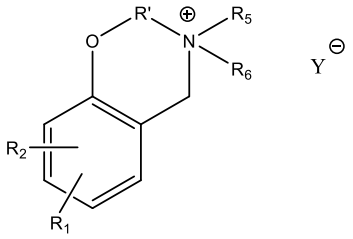
Formula Ib:



(Formula Ib)

wherein R_1 is a hydrocarbyl radical, wherein a molecular weight of the hydrocarbyl is about 200 to about 5,000; R_2 is hydrogen or a C_1-C_6 alkyl group; R' is a C1 to C4 alkyl linker; R_5 is C_1-C_6 alkyl or, together with $Y^{\ominus}$, forms a C_1-C_6 alkyl substituted $–C(O)O^{\ominus}$; R_6 is C_1-C_6 alkyl; and $Y^{\ominus}$ is an anionic group having a structure $R_8C(O)O^{\ominus}$ wherein R_8 is one of (i) together with R_5 a C_1-C_6 alkyl group or (ii) a C_1-C_6 alkyl, an aryl, a C_1-C_4 alkylene–C(O)O-R_2 or a –C(O)O-R_2 group.

[0008a] In another aspect of the present disclosure, there is provided a fuel composition comprising a major amount of fuel and a minor amount of a quaternary ammonium salt having the structure of Formula Ib;



(Formula Ib)

wherein

R_1 is a hydrocarbyl radical, wherein a molecular weight of the hydrocarbyl is 200 to 5,000;

R_2 is hydrogen or a C_1-C_6 alkyl group;

R' is a C1 to C4 alkyl linker;

R_5 is C_1-C_6 alkyl or, together with $Y^{\ominus}$, forms a C_1-C_6 alkyl substituted $–C(O)O^{\ominus}$;

R_6 is C_1-C_6 alkyl; and

$Y^{\ominus}$ is an anionic group having a structure $R_8C(O)O^{\ominus}$ wherein R_8 is one of (i) together with R_5 a C_1-C_6 alkyl group or (ii) a C_1-C_6 alkyl, an aryl, a C_1-C_4 alkylene–C(O)O-R_2 or a –C(O)O-R_2 group.

[0009] In other approaches or example, the fuel composition of the previous paragraph may be combined with other features, example, or approaches in any combination. Such examples may include one or more of the following: wherein R_1 is a hydrocarbyl radical derived from a 500 to 1500 number average molecular weight polyisobutylene polymer or oligomer, R_2 is hydrogen or a methyl group, and R' is a $-CH_2-$ group; and/or wherein R_5 is each C_1-C_6 alkyl and wherein $Y^{\ominus}$ is the anionic group having the structure $R_8C(O)O^{\ominus}$ with R_8 being the C_1-C_6 alkyl, the aryl, the C_1-C_4 alkylene–C(O)O-R_2 or the –C(O)O-R_2 group; and/or wherein R_5 is each C_1-C_6 alkyl and wherein $Y^{\ominus}$ is the anionic group having the structure $R_8C(O)O^{\ominus}$ with R_8 being the –C(O)O-R_2 group; and/or wherein the fuel is selected from diesel or gasoline; and/or wherein the fuel is diesel and includes about 20 to about 200 ppm of the quaternary ammonium salt; and/or wherein the fuel is gasoline and includes about 5 to about 20 ppm of the quaternary ammonium salt; and/or wherein the quaternary ammonium salt is derived from (i) a Mannich reaction product or derivative thereof having at least one tertiary amino group and prepared from a hydrocarbyl-substituted phenol, cresol, or derivative thereof, an aldehyde, and a hydrocarbyl amine providing the tertiary amino group and reacted with (ii) a quaternizing agent selected from the group consisting of a carboxylic or polycarboxylic acid, ester, amide, or salt thereof or halogen substituted derivative thereof; and/or wherein the hydrocarbyl amine is a C_1 to C_4 alkyl amine; and/or wherein the quaternizing agent is a diester of a polycarboxylic acid; and/or wherein the quaternizing agent is a diester of oxalic acid, phthalic

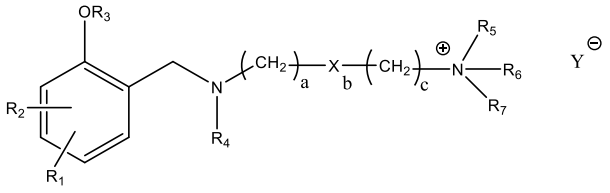
acid, maleic acid, or malonic acid, or combinations thereof; and/or wherein the quaternizing agent is a halogen substituted derivative of a carboxylic acid; and/or wherein the halogen substituted derivative of a carboxylic acid is a mono-, di-, or tri- chloro- bromo-, fluoro-, or iodo-carboxylic acid, ester, amide, or salt thereof selected from the group consisting of halogen-substituted acetic acid, propanoic acid, butanoic acid, isopropanoic acid, isobutanoic acid, *tert*-butanoic acid, pentanoic acid, heptanoic acid, octanoic acid, halo-methyl benzoic acid, and isomers, esters, amides, and salts thereof; and/or wherein the quaternary ammonium salt fuel additive is an internal salt substantially devoid of free anion species.

[00010] In yet another approach or example, the use of any example of the additive or fuel composition is described herein to provide improved engine performance such as a power recovery of about 5 percent or greater, about 10 percent or greater, or about 40 percent or greater as measured by a CEC F-98-08 test as described herein.

DETAILED DESCRIPTION

[00011] The present disclosure provides fuel additives including a Mannich-based quaternary ammonium salt formed by reacting an alkylating or quaternizing agent with a Mannich-based tertiary amine. Also provided herein are fuel compositions including the novel fuel additives and methods of using or combusting a fuel including the fuel additives herein. The unique Mannich-based quaternary ammonium salts herein are beneficial because they can be made through a simple alkylation process, surprisingly achieve a high degree of quaternization, and provide improved detergency at low treat rates by making available, in some instances, a secondary nitrogen as well as a quaternized nitrogen.

[00012] In one aspect of this disclosure, an exemplary fuel additive including a Mannich-based quaternary ammonium salt compound has the structure of Formula Ia



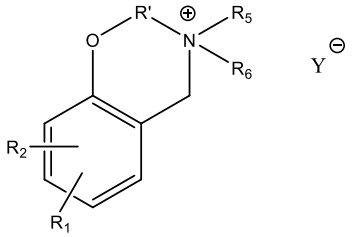
(Formula Ia)

wherein R_1 is a hydrocarbyl radical where a number average molecular weight of the hydrocarbyl is about 200 to about 5,000; R_2 is hydrogen or a C_1-C_6 alkyl group; R_3 is hydrogen

CLAIMS

WHAT IS CLAIMED IS:

1. A quaternary ammonium salt fuel additive comprising the structure of Formula Ib



(Formula Ib)

wherein

R_1 is a hydrocarbyl radical, wherein a molecular weight of the hydrocarbyl is 200 to 5,000;

R_2 is hydrogen or a C_1-C_6 alkyl group;

R' is a C_1 to C_4 alkyl linker;

R_5 is C_1-C_6 alkyl or, together with $Y^{\ominus}$, forms a C_1-C_6 alkyl substituted $-C(O)O^{\ominus}$;

R_6 is C_1-C_6 alkyl; and

$Y^{\ominus}$ is an anionic group having a structure $R_8C(O)O^{\ominus}$ wherein R_8 is one of (i) together with R_5 a C_1-C_6 alkyl group or (ii) a C_1-C_6 alkyl, an aryl, a C_1-C_4 alkylene–C(O)O-R_2 or a –C(O)O-R_2 group.

2. The quaternary ammonium salt fuel additive of claim 1, wherein R_1 is a hydrocarbyl radical derived from polyisobutylene polymer or oligomer, which has a number average molecular weight of 500 to 1500, R_2 is hydrogen or a methyl group, and R' is a -CH_2- group.

3. The quaternary ammonium salt fuel additive of claim 2, wherein R_5 is C_1-C_6 alkyl and wherein $Y^{\ominus}$ is the anionic group having the structure $R_8C(O)O^{\ominus}$ with R_8 being the C_1-C_6 alkyl, the aryl, the C_1-C_4 alkylene–C(O)O-R_2 or the –C(O)O-R_2 group; or wherein R_5 is C_1-C_6 alkyl and wherein $Y^{\ominus}$ is the anionic group having the structure $R_8C(O)O^{\ominus}$ with R_8 being the –C(O)O-R_2 group.

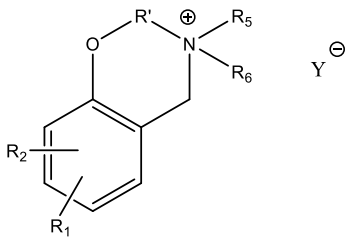
4. The quaternary ammonium salt fuel additive of claim 1, wherein the quaternary ammonium salt fuel additive is derived from (i) a Mannich reaction product or derivative thereof having at least one tertiary amino group and prepared from a hydrocarbyl-substituted phenol, cresol, or derivative thereof, an aldehyde, and a hydrocarbyl amine providing the tertiary amino group and reacted with (ii) a quaternizing agent selected from the group consisting of a carboxylic or polycarboxylic acid, ester, amide, or salt thereof or halogen substituted derivative thereof.

5. The quaternary ammonium salt fuel additive of claim 4, wherein the hydrocarbyl amine is a C_1 to C_4 alkyl amine; and/or wherein the quaternizing agent is a diester of a dicarboxylic acid; and/or wherein the quaternizing agent is a diester of oxalic acid, phthalic acid, maleic acid, or malonic acid, or combinations thereof; and/or wherein the quaternizing agent is a halogen substituted derivative of a carboxylic acid.

6. The quaternary ammonium salt fuel additive of claim 5, wherein the halogen substituted derivative of a carboxylic acid is a mono-, di-, or tri- chloro- bromo-, fluoro-, or iodo-carboxylic acid, ester, amide, or salt thereof selected from the group consisting of halogen-substituted acetic acid, propanoic acid, butanoic acid, isopropanoic acid, isobutanoic acid, *tert*-butanoic acid, pentanoic acid, heptanoic acid, octanoic acid, halo-methyl benzoic acid, and isomers, esters, amides, and salts thereof.

7. The quaternary ammonium salt fuel additive of claim 6, wherein the quaternary ammonium salt fuel additive is an internal salt substantially devoid of free anion species.

8. A fuel composition comprising a major amount of fuel and a minor amount of a quaternary ammonium salt having the structure of Formula Ib;



(Formula Ib)

wherein

R_1 is a hydrocarbyl radical, wherein a molecular weight of the hydrocarbyl is 200 to 5,000;

R_2 is hydrogen or a C_1-C_6 alkyl group;

R' is a C1 to C4 alkyl linker;

R_5 is C_1-C_6 alkyl or, together with $Y^{\ominus}$, forms a C_1-C_6 alkyl substituted $–C(O)O^{\ominus}$;

R_6 is C_1-C_6 alkyl; and

$Y^{\ominus}$ is an anionic group having a structure $R_8C(O)O^{\ominus}$ wherein R_8 is one of (i) together with R_5 a C_1-C_6 alkyl group or (ii) a C_1-C_6 alkyl, an aryl, a C_1-C_4 alkylene–C(O)O-R_2 or a –C(O)O-R_2 group.

9. The fuel composition of claim 8, wherein R_1 is a hydrocarbyl radical derived from a 500 to 1500 number average molecular weight polyisobutylene polymer or oligomer, R_2 is hydrogen or a methyl group, and R' is a -CH_2- group.

10. The fuel composition of claim 9, wherein R_5 is each C_1-C_6 alkyl and wherein $Y^{\ominus}$ is the anionic group having the structure $R_8C(O)O^{\ominus}$ with R_8 being the C_1-C_6 alkyl, the aryl, the C_1-C_4 alkylene–C(O)O-R_2 or the –C(O)O-R_2 group; or wherein R_5 is each C_1-C_6 alkyl and wherein $Y^{\ominus}$ is the anionic group having the structure $R_8C(O)O^{\ominus}$ with R_8 being the –C(O)O-R_2 group.

11. The fuel composition of claim 8, wherein the fuel is diesel and includes 20 to 200 ppm of the quaternary ammonium salt or wherein the fuel is gasoline and includes 5 to 20 ppm of the quaternary ammonium salt.

12. The fuel composition of claim 8, wherein the quaternary ammonium salt is derived from (i) a Mannich reaction product or derivative thereof having at least one tertiary amino group and prepared from a hydrocarbyl-substituted phenol, cresol, or derivative thereof, an aldehyde, and a hydrocarbyl amine providing the tertiary amino group and reacted with (ii) a quaternizing agent selected from the group consisting of a carboxylic or polycarboxylic acid, ester, amide, or salt thereof or halogen substituted derivative thereof.

13. The fuel composition of claim 12, wherein the hydrocarbyl amine is a C_1 to C_4 alkyl amine.

14. The fuel composition of claim 13, wherein the quaternizing agent is a diester of a polycarboxylic acid.

15. The fuel composition of claim 14, wherein the quaternizing agent is a diester of oxalic acid, phthalic acid, maleic acid, or malonic acid, or combinations thereof.