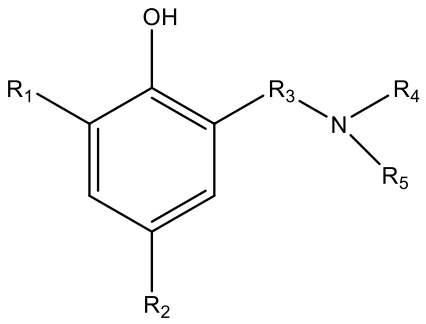
SUMMARY

[0003a] In a first aspect of the present disclosure, there is provided a fuel additive package for a spark-ignition engine comprising:

a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol, one or more aldehydes, and one or more amines, wherein the Mannich detergent has the structure of Formula I:



(Formula I)

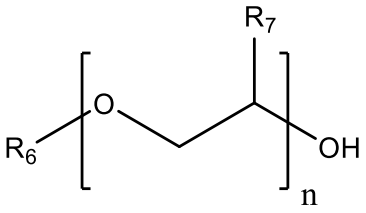
wherein R_1 is hydrogen or a C1 to C4 alkyl group, R_2 is a hydrocarbyl group having a number average molecular weight of 500 to 3000, R_3 is a C1 to C4 alkylene or alkenyl group, and R_4 and R_5 are, independently, hydrogen, a C1 to C12 alkyl group, or a C1 to C4 alkyl amino C1-C12 alkyl group;

a quaternary ammonium salt additive having the structure of Formula II

$$[(R_{10})(R_{11})N\text{-}(CH_2)_n\text{-}X_m\text{-}(CH_2)_n\text{-}X_m\text{-}(CH_2)_n\text{-}N^{\oplus}(R_7)(R_8)(R_9)]\ M^{\ominus} \qquad \text{(Formula II)}$$

wherein each X is a bivalent moiety selected from the group consisting of -O-, -N(R_{12})-, -C(O)-, -C(O)O-, or -C(O)NR_{12}; each R_7, R_8, and R_9 are independently alkyl groups containing 1 to 8 carbon atoms; R_{10} and R_{11} are independently selected from hydrogen, an alkyl group, an acyl group, or a hydrocarbyl substituted acyl group, the hydrocarbyl substituent of one or both of R_{10} and R_{11} having a number average molecular weight of 700 or greater; R_{12} is independently a hydrogen or a group selected from $C_{1\text{-}6}$ aliphatic, phenyl, or alkylphenyl; each m is independently an integer of 0 or 1 with at least one m being 1; each n is independently an integer of 1 to 10; and $M^{\ominus}$ is a carboxylate;

an alkoxylated alcohol, wherein a weight ratio of the alkoxylated alcohol to the Mannich detergent is 0.8 or less, wherein the alkoxylated alcohol is a polyether having the structure of Formula Va:



(Formula Va)

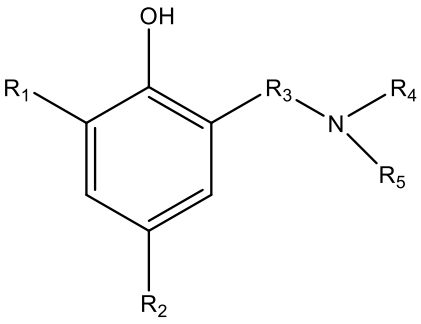
wherein R_6 is an aryl group or a linear, branched, or cyclic aliphatic group having 5 to 50 carbons, R_7 is a C1 to C4 alkyl group, and n is an integer from 5 to 100;

wherein a weight ratio of the Mannich detergent to the quaternary ammonium salt additive is 4:1 to 10:1; and

wherein the fuel additive package includes 20 to 70 weight percent of the Mannich detergent, 1 to 20 weight percent of the quaternary ammonium salt additive, and 5 to 30 weight percent of the alkoxylated alcohol.

[0003b] In another aspect of the present disclosure, there is provided a gasoline fuel composition comprising

55 to 125 ppmw of a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol, one or more aldehydes, and one or more amines, wherein the Mannich detergent has the structure of Formula I:



(Formula I)

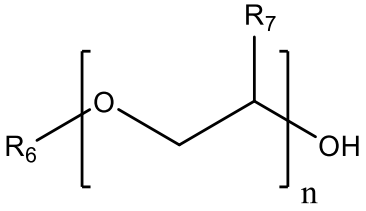
wherein R_1 is hydrogen or a C1 to C4 alkyl group, R_2 is a hydrocarbyl group having a number average molecular weight of 500 to 3000, R_3 is a C1 to C4 alkylene or alkenyl group, and R_4 and R_5 are, independently, hydrogen, a C1 to C12 alkyl group, or a C1 to C4 alkyl amino C1-C12 alkyl group;

4 to 15 ppmw of a quaternary ammonium salt additive has the structure of Formula II

$[(R_{10})(R_{11})N\text{-}(CH_2)_n\text{-}X_m\text{-}(CH_2)_n\text{-}X_m\text{-}(CH_2)_n\text{-}N^{\oplus}(R_7)(R_8)(R_9)]\ M^{\ominus}$ (Formula II)

wherein each X is a bivalent moiety selected from the group consisting of -O-, -N(R_{12})-, -C(O)-, -C(O)O-, or -C(O)NR_{12}; each R_7, R_8, and R_9 are independently alkyl groups containing 1 to 8 carbon atoms; R_{10} and R_{11} are independently selected from hydrogen, an alkyl group, an acyl group, or a hydrocarbyl substituted acyl group, the hydrocarbyl substituent of one or both of R_{10} and R_{11} having a number average molecular weight of 700 or greater; R_{12} is independently a hydrogen or a group selected from $C_{1\text{-}6}$ aliphatic, phenyl, or alkylphenyl; each m is independently an integer of 0 or 1 with at least one m being 1; each n is independently an integer of 1 to 10; and $M^{\ominus}$ is a carboxylate; and

15 to 40 ppmw of an alkoxylated alcohol, wherein a weight ratio of the alkoxylated alcohol to the Mannich detergent is 0.8 or less, wherein the alkoxylated alcohol is a polyether having the structure of Formula Va:



(Formula Va)

wherein R_6 is an aryl group or a linear, branched, or cyclic aliphatic group having 5 to 50 carbons, R_7 is a C1 to C4 alkyl group, and n is an integer from 5 to 100; and

wherein a weight ratio of the Mannich detergent to the quaternary ammonium salt additive is 4:1 to 10:1.

[0003c] In yet another aspect of the present disclosure, there is provided a method of improving the injector performance of a gasoline direct injection (GDI) engine, the method comprising:

operating the gasoline direct injection engine on a fuel composition containing a major amount of a gasoline fuel and a minor amount of the fuel additive package as disclosed herein; and

wherein the fuel additive package in the gasoline fuel improves the injector performance of the gasoline direct injection engine.

[0004] In one example, a fuel additive package, a fuel, or a method of providing improved engine performance is provided herein.

[0005] In one example or approach, a fuel additive package for an internal combustion engine is described herein to provide the improved engine performance and includes a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol, one or more aldehydes, and one or more amines; and a quaternary ammonium salt additive having the structure of Formula II

$$[(R_{10})(R_{11})N\text{-}(CH_2)_n\text{-}X_m\text{-}(CH_2)_n\text{-}X_m\text{-}(CH_2)_n\text{-}N^{\oplus}(R_7)(R_8)(R_9)]\ M^{\ominus} \qquad \text{(Formula II)}$$

wherein each X is a bivalent moiety selected from the group consisting of -O-, -N(R_{12})-, -C(O)-, -C(O)O-, or -C(O)NR_{12}; each R_7, R_8, and R_9 are independently alkyl groups containing 1 to 8 carbon atoms; R_{10} and R_{11} are independently selected from hydrogen, an alkyl group, an acyl group, or a hydrocarbyl substituted acyl group (optionally, R_{10} and R_{11} together with the N atom to which they are attached, combine to form a ring moiety (such as a succinimide)), the hydrocarbyl substituent of one or both of R_{10} and R_{11} have a number average molecular weight of about 700 or greater (as further described herein); R_{12} is independently a hydrogen or a group selected from $C_{1\text{-}6}$ aliphatic, phenyl, or alkylphenyl; each m is independently an integer of 0 or 1 with at least one m being 1; each n is independently an integer of 1 to 10; and $M^{\ominus}$ is a carboxylate. The above-mentioned internal combustion engine can be a spark-ignition engine or a diesel engine.

[0006] In another example or approach, the fuel additive package of the previous paragraph may include optional features or examples in any combination. These optional features or examples include one or more of the following: further comprising an alkoxylated alcohol; and/or wherein a weight ratio of the alkoxylated alcohol to the Mannich detergent is about 1.0 or less; and/or wherein the alkoxylated alcohol is a polyether prepared by reacting an alkyl alcohol or an alkylphenol with an alkylene oxide selected from ethylene oxide, propylene oxide, butylene oxide, copolymers thereof, or combinations thereof; and/or wherein a weight ratio of the Mannich detergent to the quaternary ammonium salt additive is about 4:1 to about 100:1; and/or wherein the Mannich detergent has the structure of Formula I:

wherein the fuel additive package includes about 20 to about 60 weight percent of the Mannich detergent, about 1 to about 20 weight percent of the quaternary ammonium salt additive, and about 5 to about 30 weight percent of the alkoxylated alcohol; and/or further comprising a succinimide detergent prepared by reacting a hydrocarbyl-substituted succinic acylating agent with an amine, polyamine, or alkyl amine having one or more primary, secondary, or tertiary amino groups; and/or wherein the fuel additive package includes about 0.1 to about 10 weight percent of the succinimide detergent; and/or wherein the succinimide detergent is a hydrocarbyl substituted mono-succinimide detergent, a hydrocarbyl substituted bis-succinimide detergent, or a combination thereof; and/or further comprising one or more of a demulsifier, a corrosion inhibitor, an antiwear additive, an antioxidant, a metal deactivator, an antistatic additive, a dehazer, an antiknock additive, a lubricity additive, and/or a combustion improver.

[0007] In another example, a fuel including any example of the above described fuel additive package is provided herein for improved engine performance. In one example or approach, a gasoline fuel composition is provided that includes about 15 to about 300 ppmw of a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol, one or more aldehydes, and one or more amines; about 0.1 to about 50 ppmw of a quaternary ammonium salt additive (or about 0.1 to about 30 ppmw) has the structure of Formula II

$$[(R_{10})(R_{11})N\text{-}(CH_2)_n\text{-}X_m\text{-}(CH_2)_n\text{-}X_m\text{-}(CH_2)_n\text{-}N^{\oplus}(R_7)(R_8)(R_9)]\ M^{\ominus} \qquad \text{(Formula II)}$$

wherein each X is a bivalent moiety selected from the group consisting of -O-, -N(R_{12})-, -C(O)-, -C(O)O-, or -C(O)NR_{12}; each R_7, R_8, and R_9 are independently alkyl groups containing 1 to 8 carbon atoms; R_{10} and R_{11} are independently selected from hydrogen, an alkyl group, an acyl group, or a hydrocarbyl substituted acyl group (optionally, R_{10} and R_{11} together with the N atom to which they are attached, combine to form a ring moiety (such as a succinimide)), the hydrocarbyl substituent of one or both of R_{10} and R_{11} having a number average molecular weight of about 700 or greater; R_{12} is independently a hydrogen or a group selected from $C_{1\text{-}6}$ aliphatic, phenyl, or alkylphenyl; each m is independently an integer of 0 or 1 with at least one m being 1; each n is independently an integer of 1 to 10; and $M^{\ominus}$ is a carboxylate; and about 5 to about 150 ppmw of an alkoxylated alcohol. In another example or approach, a diesel fuel composition is provided that includes about 15 to about 500 ppmw of a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol, one or more aldehydes, and one or more

amines; about 0.1 to about 200 ppmw of a quaternary ammonium salt additive as described in any example above.

[0008] In other examples, the fuel of the previous Paragraph may include any example of the fuel additive package described in this Summary.

[0009] In yet other examples, a method of improving the injector performance of a gasoline direct injection (GDI) engine is described herein. In yet other examples, a method of improving the injector performance of a gasoline port fuel injection (PFI) engine is described herein. In further examples, a method of improving the injector performance of both GDI and PFI engines is described herein. Further, the use of a fuel additive package or a fuel for improving the injector performance of a GDI engine and/or a PFI engine is also described herein. In approaches or examples, the method or the use includes operating the gasoline direct injection engine on a fuel composition containing a major amount of a gasoline fuel and a minor amount of any example of the fuel additive package as described in this Summary; and wherein the fuel additive package in the gasoline fuel improves the injector performance of the gasoline direct injection engine. In other approaches, the improved injector performance is one of improved fuel flow, improved fuel economy, improved engine efficiency, or combinations thereof; and/or wherein the improved injector performance is measured by one of injector pulse width, injection duration, injector flow, or combinations thereof.

[00010] In yet other examples, a method of improving the diesel engine performance is described herein. In further examples, a method of improving the injector performance of a diesel engine. Further, the use of a fuel additive package or a fuel as described in any example herein for improving the injector performance of a diesel engine is also described herein. In approaches or examples, the method or the use includes operating the diesel engine on a fuel composition containing a major amount of a diesel fuel and a minor amount of any example of the fuel additive package as described in this Summary; and wherein the fuel additive package in the diesel fuel improves the injector performance of the diesel engine, i.e., a direct injection or indirect injection engine. In other approaches, the engine performance is one of improved fuel flow, improved fuel economy, improved engine efficiency, or combinations thereof; and/or wherein the improved injector performance is measured by one of injector pulse width, injection duration, injector flow, or combinations thereof.

[00011] The method or the use of the previous paragraphs may include optional steps,

features, or limitations in any combination thereof. Approaches or examples of the method or use may include one or more of the following: wherein the improved injector performance is one of improved fuel flow, improved fuel economy, improved engine efficiency, or combinations thereof; and/or wherein the improved injector performance is measured by one of long term fuel trim, injector pulse width, injection duration, injector flow, or combinations thereof.

BRIEF DESCRIPTION OF THE DRAWING FIGURE

[00012] FIG. 1 is a graph showing Long Term Fuel Trim (LTFT) of Comparative and Inventive fuel additives.

DETAILED DESCRIPTION

[00013] The present disclosure relates to fuel additives including combinations of Mannich detergents and quaternary ammonium salts and, in particular, Mannich detergents and high molecular weight, polyamine and/or ether amine derived hydrocarbyl-substituted quaternary ammonium salts discovered effective to provide improved engine and/or injector performance in both port fuel injection (PFI) engines as well as gasoline direct injection (GDI) engines. The fuel additives, in some approaches, may also include alkoxylated alcohols and, when included, certain ratios of the alkoxylated alcohol to the Mannich detergent. Also provided herein are fuel compositions including the novel fuel additive combinations and methods of using or combusting a fuel including the fuel additive combinations herein to achieve the improved engine and/or injector performance.

[00014] In aspects or embodiments of this disclosure, improved engine and/or injector performance of the fuel additive combinations herein may include one or more of controlling or reducing fuel injector deposits, controlling or reducing intake valve deposits, controlling or reducing combustion chamber deposits and/or controlling or reducing intake valve sticking. Improved injector performance may also be one or more of improved fuel flow, improved fuel economy, and/or improved engine efficiency as determined via one or more of long term fuel trim, injector pulse width, injection duration, and/or injector flow.

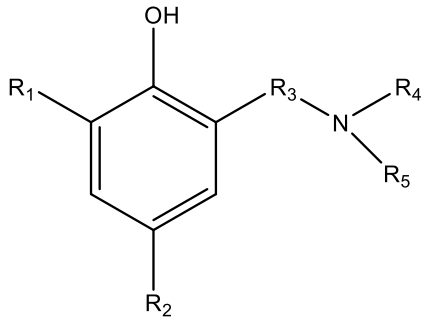
[00015] The present disclosure also relates to fuel additives including combinations of Mannich detergents and quaternary ammonium salts and, in particular, Mannich detergents and

CLAIMS

WHAT IS CLAIMED IS:

1. A fuel additive package for a spark-ignition engine comprising:

a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol, one or more aldehydes, and one or more amines, wherein the Mannich detergent has the structure of Formula I:



(Formula I)

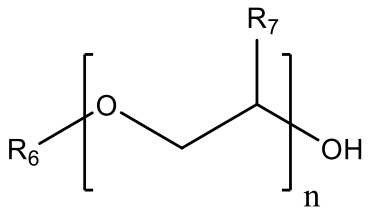
wherein R_1 is hydrogen or a C1 to C4 alkyl group, R_2 is a hydrocarbyl group having a number average molecular weight of 500 to 3000, R_3 is a C1 to C4 alkylene or alkenyl group, and R_4 and R_5 are, independently, hydrogen, a C1 to C12 alkyl group, or a C1 to C4 alkyl amino C1-C12 alkyl group;

a quaternary ammonium salt additive having the structure of Formula II

$$[(R_{10})(R_{11})N\text{-}(CH_2)_n\text{-}X_m\text{-}(CH_2)_n\text{-}X_m\text{-}(CH_2)_n\text{-}N^{\oplus}(R_7)(R_8)(R_9)]\ M^{\ominus} \qquad \text{(Formula II)}$$

wherein each X is a bivalent moiety selected from the group consisting of -O-, -N(R_{12})-, -C(O)-, -C(O)O-, or -C(O)NR_{12}; each R_7, R_8, and R_9 are independently alkyl groups containing 1 to 8 carbon atoms; R_{10} and R_{11} are independently selected from hydrogen, an alkyl group, an acyl group, or a hydrocarbyl substituted acyl group, the hydrocarbyl substituent of one or both of R_{10} and R_{11} having a number average molecular weight of 700 or greater; R_{12} is independently a hydrogen or a group selected from $C_{1\text{-}6}$ aliphatic, phenyl, or alkylphenyl; each m is independently an integer of 0 or 1 with at least one m being 1; each n is independently an integer of 1 to 10; and $M^{\ominus}$ is a carboxylate;

an alkoxylated alcohol, wherein a weight ratio of the alkoxylated alcohol to the Mannich detergent is 0.8 or less, wherein the alkoxylated alcohol is a polyether having the structure of Formula Va:



(Formula Va)

wherein R_6 is an aryl group or a linear, branched, or cyclic aliphatic group having 5 to 50 carbons, R_7 is a C1 to C4 alkyl group, and n is an integer from 5 to 100;

wherein a weight ratio of the Mannich detergent to the quaternary ammonium salt additive is 4:1 to 10:1; and

wherein the fuel additive package includes 20 to 70 weight percent of the Mannich detergent, 1 to 20 weight percent of the quaternary ammonium salt additive, and 5 to 30 weight percent of the alkoxylated alcohol.

2. The fuel additive package of claim 1, wherein the alkoxylated alcohol is a polyether prepared by reacting an alkyl alcohol or an alkylphenol with an alkylene oxide selected from ethylene oxide, propylene oxide, butylene oxide, copolymers thereof, or combinations thereof.

3. The fuel additive package of claim 1, wherein R_{10} and R_{11} of the quaternary ammonium salt of Formula II, together with the nitrogen atom to which they are attached, combine to form a ring moiety.

4. The fuel additive package of claim 1, wherein the carboxylate of the quaternary ammonium salt of Formula II is oxalate, salicylate, or combinations thereof.

5. The fuel additive package of claim 4, wherein X of Formula II is –O- or –NH-.

6. The fuel additive package of claim 5, wherein the quaternary ammonium salt is derived from 3-(2-(dimethylamino)ethoxy)propylamine, N,N-dimethyldipropylenetriamine, or mixtures thereof.

7. The fuel additive package of claim 1, wherein R_{10} and R_{11} of the quaternary ammonium salt of Formula II, together with the nitrogen atom to which they are attached, combine to form a hydrocarbyl substituted succinimide.

8. The fuel additive package of claim 7, wherein the hydrocarbyl substituent has a number average molecular weight of 700 to 2,500.

9. The fuel additive package of claim 1, wherein X moiety of the quaternary ammonium salt of Formula II is an oxygen atom and wherein R_{10} and R_{11} of the quaternary ammonium salt, together with the nitrogen atom to which they are attached, combine to form a hydrocarbyl substituted succinimide with the hydrocarbyl substituent having a number average molecular weight of 700 to 1,500 as measured by GPC using polystyrene as a calibration reference.

10. The fuel additive package of claim 1, wherein the fuel additive package includes 20 to 60 weight percent of the Mannich detergent.

11. The fuel additive package of claim 1, further comprising a succinimide detergent prepared by reacting a hydrocarbyl-substituted succinic acylating agent with an amine, polyamine, or alkyl amine having one or more primary, secondary, or tertiary amino groups.

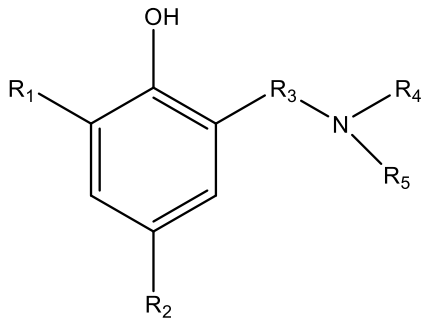
12. The fuel additive package of claim 11, wherein the fuel additive package includes 0.1 to 10 weight percent of the succinimide detergent.

13. The fuel additive package of claim 12, wherein the succinimide detergent is a hydrocarbyl substituted mono-succinimide detergent, a hydrocarbyl substituted bis-succinimide detergent, or a combination thereof.

14. The fuel additive package of claim 12, further comprising one or more of a demulsifier, a corrosion inhibitor, an antiwear additive, an antioxidant, a metal deactivator, an antistatic additive, a dehazer, an antiknock additive, a lubricity additive, and/or a combustion improver.

15. A gasoline fuel composition comprising

55 to 125 ppmw of a Mannich detergent including the reaction product of a hydrocarbyl-substituted phenol, one or more aldehydes, and one or more amines, wherein the Mannich detergent has the structure of Formula I:



(Formula I)

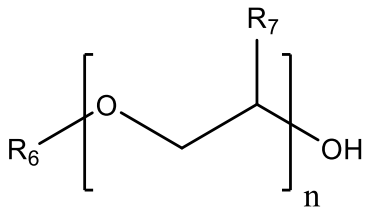
wherein R_1 is hydrogen or a C1 to C4 alkyl group, R_2 is a hydrocarbyl group having a number average molecular weight of 500 to 3000, R_3 is a C1 to C4 alkylene or alkenyl group, and R_4 and R_5 are, independently, hydrogen, a C1 to C12 alkyl group, or a C1 to C4 alkyl amino C1-C12 alkyl group;

4 to 15 ppmw of a quaternary ammonium salt additive has the structure of Formula II

$$[(R_{10})(R_{11})N\text{-}(CH_2)_n\text{-}X_m\text{-}(CH_2)_n\text{-}X_m\text{-}(CH_2)_n\text{-}N^{\oplus}(R_7)(R_8)(R_9)]\ M^{\ominus} \qquad \text{(Formula II)}$$

wherein each X is a bivalent moiety selected from the group consisting of -O-, -N(R_{12})-, -C(O)-, -C(O)O-, or -C(O)NR_{12}; each R_7, R_8, and R_9 are independently alkyl groups containing 1 to 8 carbon atoms; R_{10} and R_{11} are independently selected from hydrogen, an alkyl group, an acyl group, or a hydrocarbyl substituted acyl group, the hydrocarbyl substituent of one or both of R_{10} and R_{11} having a number average molecular weight of 700 or greater; R_{12} is independently a hydrogen or a group selected from $C_{1\text{-}6}$ aliphatic, phenyl, or alkylphenyl; each m is independently an integer of 0 or 1 with at least one m being 1; each n is independently an integer of 1 to 10; and $M^{\ominus}$ is a carboxylate; and

15 to 40 ppmw of an alkoxylated alcohol, wherein a weight ratio of the alkoxylated alcohol to the Mannich detergent is 0.8 or less, wherein the alkoxylated alcohol is a polyether having the structure of Formula Va:



(Formula Va)

wherein R_6 is an aryl group or a linear, branched, or cyclic aliphatic group having 5 to 50 carbons, R_7 is a C1 to C4 alkyl group, and n is an integer from 5 to 100; and

wherein a weight ratio of the Mannich detergent to the quaternary ammonium salt additive is 4:1 to 10:1.

16. A method of improving the injector performance of a gasoline direct injection (GDI) engine, the method comprising:

operating the gasoline direct injection engine on a fuel composition containing a major amount of a gasoline fuel and a minor amount of the fuel additive package of claim 1; and

wherein the fuel additive package in the gasoline fuel improves the injector performance of the gasoline direct injection engine.

17. The method of claim 16, wherein the improved injector performance is one of improved fuel flow, improved fuel economy, improved engine efficiency, or combinations thereof.

18. The method of claim 17, wherein the improved injector performance is measured by one of injector pulse width, injection duration, injector flow, or combinations thereof.