

REDUCING FRICTION IN COMBUSTION ENGINES THROUGH FUEL ADDITIVES

TECHNICAL FIELD

[001] This disclosure relates to fuel additive compositions. More specifically, the disclosure relates to friction modifier additives that can be added to fuel to improve fuel efficiency of internal combustion engines.

BACKGROUND

[002] There has been considerable effort in recent years to improve the fuel economy of motor vehicles. In general, the efficiency of automotive engines is greatly enhanced by the presence of effective lubrication, particularly at the interface of moving parts that are prone to high friction and excessive wear.

[003] Thus, one approach to improving fuel economy has been developing lubricants and lubricating oil additives that reduce engine friction and thus reduce energy requirements. However, improvements in fuel efficiency obtained with lubricating oil friction reducing additives have been modest and can be difficult to ascertain.

[004] Some of these efforts have focused on friction modifiers. Friction modifiers have been used in limited slip gear oils, automatic transmission fluids, slideway lubricants and multipurpose tractor fluids. In particular, with the desire for increased fuel economy, friction modifiers have been added to automotive crankcase lubricants.

[005] These friction modifiers generally operate at boundary layer conditions at temperatures where anti-wear and extreme pressure additives are not yet reactive by forming a thin mono-molecular layers of physically adsorbed polar oil-soluble products or reaction layers which exhibit a significantly lower friction compared to typical anti-wear or extreme pressure agents. However, under more severe conditions and in mixed lubrication regime these friction modifiers are added with an anti-wear or extreme pressure agent. The most common type of anti-wear or extreme pressure agent is a zinc dithiophosphate (ZnDTP or ZDDP). ZDDP limit wear by forming a thick protective tribofilm on rubbing surfaces.

[006] Although ZDDP has been widely in use in motor vehicles for many decades, some recent studies have shown that phosphorus-based antiwear films can cause significant increase in friction in thin film, high-pressure, lubricated contacts. This, in turn, can have a negative effect on fuel efficiency.

[007] Friction modifiers are known lubricating oil additives that can reduce boundary friction by adsorbing or reacting on metal surfaces to form thin low-shear-strength films.

[008] Since the conditions in an internal combustion chamber are substantially different from, and much more severe than, those in a crankcase, the fact that a particular additive or class of additives has benefited the performance of a lubricating oil in an internal combustion engine does not necessarily mean that benefits will be gained by using the same types of compounds as additives in the fuel. Thus, there is a need to develop fuel additives that can reduce friction and/or improve fuel economy.

SUMMARY

[009] Provided herein are compositions that can be added to fuel as additives to provide an enhancement of friction reduction and/or fuel economy of an internal combustion engine. These fuel additives include a friction modifier and a metal chelating agent that interact synergistically to provide an unexpected level of performance.

[010] One example of the present invention includes a fuel composition comprising greater than 50 wt % of a hydrocarbon fuel boiling in the gasoline or diesel range; a minor amount a zinc chelator; and a minor amount of a friction modifier, wherein the friction modifier includes at least one polar group.

[011] Another example of the present invention includes a fuel concentrate composition comprising (1) from 90 to 30 wt % of an organic solvent boiling in a range of from 65°C to 205°C and (2) from 10 to 70 wt % of fuel efficiency improver including a zinc chelator and a friction modifier having at least one polar group.

[012] Yet another example of the present invention includes a method of improving fuel efficiency in a spark-ignited combustion engine, the method

comprising supplying to the engine a fuel composition comprising a zinc chelator and a friction modifier having at least one polar group.

BRIEF DESCRIPTION OF DRAWINGS

[013] FIG. 1 shows a graph that summarizes the effect of several fuel additives on fuel consumption at various engine conditions.

DETAILED DESCRIPTION

[014] To facilitate understanding of the disclosure set forth herein, a number of terms are defined below. Unless defined otherwise, all technical and scientific terms used herein generally have the same meaning as commonly understood by one of ordinary skill in the art to which this disclosure belongs.

[015] "Gasoline" or "gasoline boiling range components" refers to a composition containing at least predominantly C₄-C₁₂ hydrocarbons. In one embodiment, gasoline or gasoline boiling range components is further defined to refer to a composition containing at least predominantly C₄-C₁₂ hydrocarbons and further having a boiling range of from about 100°F (37.8°C) to about 400°F (204°C). In an alternative embodiment, gasoline or gasoline boiling range components is defined to refer to a composition containing at least predominantly C₄-C₁₂ hydrocarbons, having a boiling range of from about 100°F (37.8°C) to about 400°F (204°C), and further defined to meet ASTM D4814.

[016] The term "diesel" refers to middle distillate fuels containing at least predominantly C₁₀-C₂₅ hydrocarbons. In one embodiment, diesel is further defined to refer to a composition containing at least predominantly C₁₀-C₂₅ hydrocarbons, and further having a boiling range of from about 165.6°C (330°F) to about 371.1°C (700°F). In an alternative embodiment, diesel is as defined above to refer to a composition containing at least predominantly C₁₀-C₂₅ hydrocarbons, having a boiling range of from about 165.6°C (330°F) to about 371.1°C (700°F), and further defined to meet ASTM D975.

[017] The term "oil soluble" means that for a given additive, the amount needed to provide the desired level of activity or performance can be incorporated by being dissolved, dispersed or suspended in an oil of lubricating viscosity. Usually, this means that at least 0.001% by weight of the additive can be incorporated in a lubricating oil composition. The term "fuel soluble" is an analogous expression for additives dissolved, dispersed or suspended in fuel.

[018] A "minor amount" means less than 50 wt % of a composition, expressed in respect of the stated additive and in respect of the total weight of the composition, reckoned as active ingredient of the additive.

[019] An "engine" or a "combustion engine" is a heat engine where the combustion of fuel occurs in a combustion chamber. An "internal combustion engine" is a heat engine where the combustion of fuel occurs in a confined space ("combustion chamber"). A "spark ignition engine" is a heat engine where the combustion is ignited by a spark, usually from a spark plug. This is contrast to a "compression-ignition engine," typically a diesel engine, where the heat generated from compression together with injection of fuel is sufficient to initiate combustion without an external spark.

[020] A "zinc chelator" refers to any substance that is able to chelate a zinc (Zinc^{2+}) ion.

[021] This disclosure describes additive compositions that can be added to fuel to enhance friction reduction and/or improve fuel efficiency of internal combustion engines. The additive composition ("fuel efficiency improver") comprises at least two components: a friction modifier and a zinc chelating agent. When formulated in accordance with this disclosure, these components take advantage of a previously unknown synergy to provide a greater than expected improvement in friction reduction and/or fuel efficiency in engines.

[022] It is believed that additives added to fuel may be transferred into the lubricant in the engine piston ring zone where it may reduce friction and wear and thus improve economy. However, it may not necessarily be the case that additives

added to lubricant are transferred to fuel. Thus, friction modifiers can provide fuel economy by reducing friction in the combustion chamber of an internal combustion engine.

Zinc Chelator

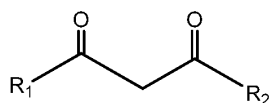
[023] The chelators employed in the present fuel composition include organic molecules that can chelate zinc. In general, these chelators can form an inner complex with zinc by way of chelate ring formation. The zinc chelator may vary in its denticity, that is, the number of atoms of the chelator which binds to zinc. For example, the zinc chelator may be bidentate.

[024] Without being limited by theory, it is believed that zinc chelators of the present invention can limit the friction caused or induced by ZDDP in an engine environment. The limiting effect can be synergistically enhanced when friction modifiers of the present invention are also present. While the mechanism is not fully understood, It is believed that the friction modifiers of the present invention can form a friction-reducing film on a zinc phosphate surface and/or stabilize the zinc chelator in an engine environment.

[025] In some embodiments, the zinc chelator may be fuel soluble. In other embodiments, the zinc chelator may not be oil soluble. In the absence of the friction modifier of the present invention, the lack of oil solubility may prevent the zinc chelator from chelating with zinc species in a lubricant environment.

[026] The zinc chelators of the present invention include dicarbonyl compounds, bidentate nitrogen compounds, multidentate nitrogen compounds, amino acids, citrate esters, carboxylate salts, amine salts, or a suitable salt thereof. The metal chelator is present in about 25 to about 5000 ppm of the fuel composition.

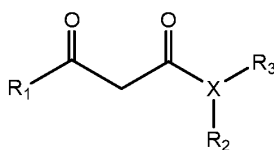
[027] Dicarbonyl compounds can have the structure shown in Formula 1, wherein R_1 and R_2 is independently aliphatic, aliphatic branched, cyclic aliphatic, aromatic, substituted aromatic, or unsaturated (e.g., olefinic) moiety.



Formula 1

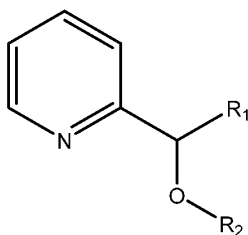
[028] A specific example of a dicarbonyl chelator is acetyl acetone. When acetyl acetone acts as a bidentate ligand, it is often referred to as “acac.”

[029] Other dicarbonyl compounds include chelators having the structure shown in Formula 2, wherein X is O or N and has correct valence, R₁, R₂, and R₃ are independently aliphatic, aliphatic branched, cyclic aliphatic, aromatic, substituted aromatic, or unsaturated (e.g., olefinic) moiety. Additionally, R₂ and R₃ may also be H (enough to satisfy valence of X). Specific examples include ethyl acetoacetate, acetoacetic ester, and acetoacetic amide.



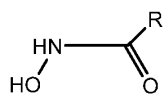
Formula 2

[030] Some bidentate nitrogen compounds will generally have at least one nitrogen atom that can directly coordinate to zinc or at least stabilize the coordination to zinc to a nearby atom. For example, the bidentate nitrogen compound can have a structure shown in Formula 3 below, where R₁ and R₂ are independently aliphatic, aliphatic branched, cyclic aliphatic, aromatic, substituted aromatic, unsaturated (e.g., olefinic) moiety, or H. Both the nitrogen and oxygen can coordinate to zinc to form a chelate ring.

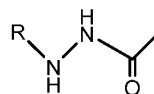


Formula 3

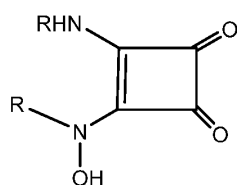
[031] Other bidentate nitrogen compounds may also be contemplated. Specific examples of bidentate nitrogen compounds include hydroxamic acid (Formula 4), hydrazide (Formula 5), squaric acid (Formula 6), carbamoylphosphonate (Formula 7), oxazoline (Formula 8) and N-hydroxyurea (Formula 9), where R is independently aliphatic, aliphatic branched, cyclic aliphatic, aromatic, substituted aromatic, unsaturated (e.g., olefinic) moiety or H.



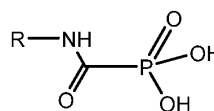
Formula 4



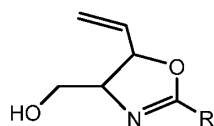
Formula 5



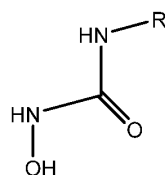
Formula 6



Formula 7



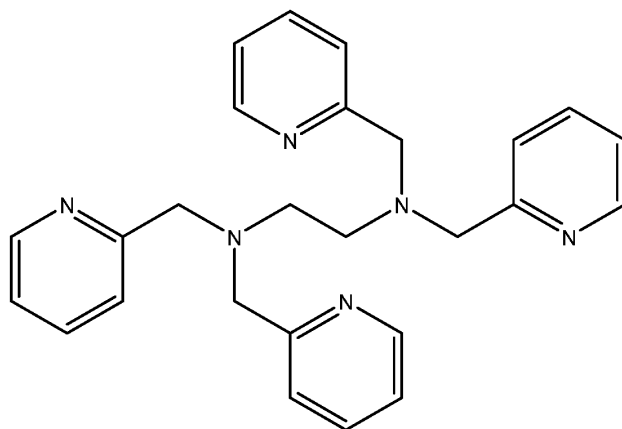
Formula 8



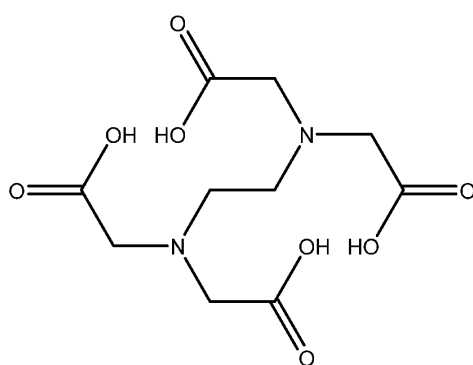
Formula 9

[032] Other specific examples of bidentate nitrogen chelators include amino methyl compounds, methyl pyridyl compounds, quinolyl compounds, pyrazyl compounds, 5 membered N-heterocyclic compounds (e.g., pyrrole/ pyrrolidine, imidazole/imidazoline, triazole) and diethanolisostearamide.

[033] Multidentate nitrogen compounds may also be compatible with the present invention. Specific examples of these include N,N,N',N'-tetrakis(2-pyridinylmethyl)-1,2-ethanediamine (Formula 10) and ethylenediaminetetraacetic acid (Formula 11).



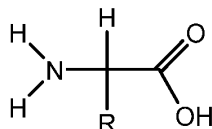
Formula 10



Formula 11

Amino Acids

[034] Amino acids include those that can be represented by the following general formula:

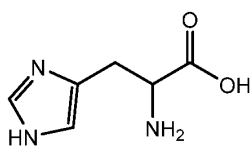


Formula 12

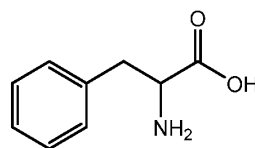
wherein R is an “aliphatic” or “aromatic” side chain. Amino acid side chains can be broadly classified as aromatic or aliphatic. An aromatic side chain includes an aromatic ring. Examples of amino acids with aromatic side chains include for example, histidine (**Formula 13**), phenylalanine (**Formula 14**), tyrosine (**Formula 15**), tryptophan (**Formula 16**) and the like. Non-aromatic side chains are broadly grouped as “aliphatic” and include, for example, alanine (**Formula 17**), glycine (**Formula 18**), cysteine (**Formula 19**), and the like.

[035] The amino acid(s) can be natural and/or non-natural α -amino acids. Natural amino acids are those encoded by the genetic code, as well as amino acids derived therefrom. These include, for example, hydroxyproline (**Formula 20**), γ -carboxyglutamate (**Formula 21**), and citrulline (**Formula 22**). In this specification, the term “amino acid” also includes amino acid analogs and mimetics. Analogs are compounds having the same general structure of a natural amino acid, except that the R group is not one found among the natural amino acids.

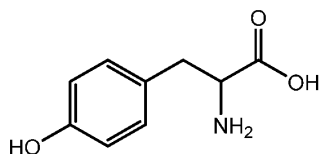
[036] Representative examples of analogs of naturally occurring amino acids include homoserine (**Formula 23**), norleucine (**Formula 24**), homoproline (**Formula 25**) and proline (**Formula 26**). An amino acid mimetic is a compound that has a structure different from the general chemical structure of an α -amino acid but functions in a manner similar to one. The amino acid may be an L- or D-amino acid. Representative structures are shown below.



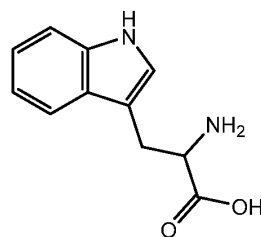
Formula 13



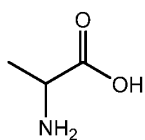
Formula 14



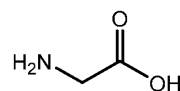
Formula 15



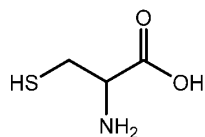
Formula 16



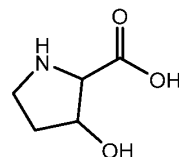
Formula 17



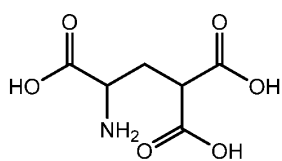
Formula 18



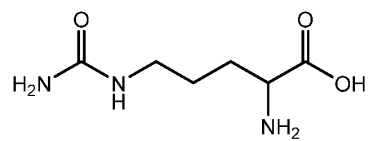
Formula 19



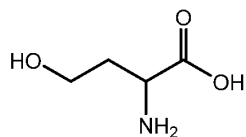
Formula 20



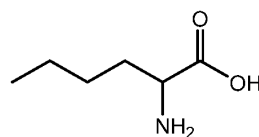
Formula 21



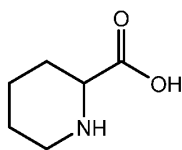
Formula 22



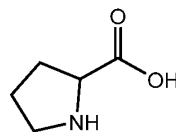
Formula 23



Formula 24



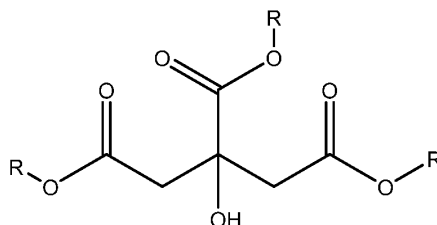
Formula 25



Formula 26

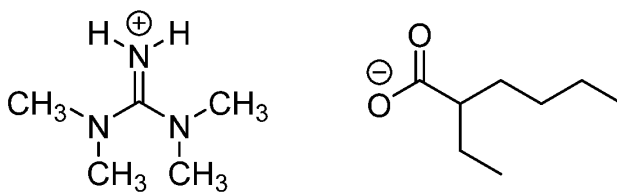
Miscellaneous Zinc Chelators

[037] Zinc chelators can be made from carboxylate esters with variable non-polar groups. Zinc chelators can also include multi-functional esters including citrate esters. Citrate esters can have the structure shown in Formula 27 wherein R is alkyl, alkenyl, cycloalkyl, aromatic, or substituted aromatic moiety.



Formula 27

[038] Specific examples of carboxylate salts include 1,1,3,3-tetramethylguanidine salt of 2-ethylhexanoic acid (TMG/2-EH), where TMG/2-EH is shown in Formula 28.



Formula 28

Friction Modifiers

[039] Friction modifiers are additives that can reduce friction and/or wear in machine components. The friction modifiers of the present invention include organic

friction modifiers having at least one polar group. These friction modifiers are typically bifunctional in that the friction modifier will also generally have a long chain and/or aromatic non-polar group.

[040] The polar group can be an alcohol moiety, amide moiety, amine moiety, ester moiety, and the like. In some embodiments, the friction modifier can have more than one polar moiety (e.g., diol, diester, alkanol amide, etc.).

[041] The friction modifier may be fuel soluble and/or oil soluble. The friction modifier of the present invention stabilizes the zinc chelator in a lubricant environment thus allowing the zinc chelator to chelate zinc and also adsorb onto a zinc phosphate tribofilm to form a friction reducing layer.

[042] Specific friction modifiers with ester moiety include esters of carboxylic acid, adipate ester, trimethylolpropane triester, polyol esters (e.g., glycerol ester, sorbitan ester, etc.), polyesters, and esters with high viscosity index (VI) and/or can change hydrodynamic friction. In some embodiments, the ester may be borated.

[043] Other compatible friction modifiers include alkanol amides (including polar group capped fatty amides and polyol amines. Specific alkanol amide includes diethanolamide.

[044] Amine friction modifiers include hydrocarbyl amines, fatty acid amines (e.g., oleylamine), and ethoxylated alkyl amines. Specific amine friction modifiers include diethanolamine and diisopropanolamine.

[045] Specific friction modifiers are described in greater detail, in for example, US7678747, US8703680, and US9371499 which are hereby incorporated by reference.

[046] In particular, polyol ester are often used as synthetic basestock oils that can be synthesized from a polyol and an acid (e.g., branched acid, linear saturated acid, polybasic acid). Examples of polyol ester include glycerol esters, sorbitan esters, and the like.

[047] A specific glycerol ester includes a glycerol monooleate (or glyceryl monooleate), a friction modifier conventionally added to lubricant compositions. For example, U.S. Pat. Nos. 5,114,603 and 4,683,069 describe lubricating oil compositions

comprising glycerol monooleate, the relevant portions of which are hereby incorporated by reference.

[048] Examples of commercially available glycerol monooleate include Priolube™ 1408 and Radasurf™ 7149 (i.e., esters of fatty acids including glycerol trioleate). In a typical commercial product, only about 50-60 mole percent of the esters produced are monoesters. The remainder are primarily diesters, with a small amount of triester.

[049] Typically, the fuel compositions of this invention contain at least 0.015 wt %, preferably 0.15 to 2.0 wt % of the friction modifier.

[050] The glycerol esters useful for this invention are fuel-soluble and are preferably prepared from C12 to C22 fatty acids or mixtures thereof such as are found in natural products. The fatty acid may be saturated or unsaturated. Certain compounds found in acids from natural sources may include licanic acid which contains one keto group. Most preferred C16 to C18 fatty acids are those of the formula R—COOH wherein R is alkyl or alkenyl. Preferred fatty acids are oleic, stearic, isostearic, palmitic, myristic, palmitoleic, linoleic, lauric, linolenic, and eleostearic, and the acids from the natural products tallow, palm oil, olive oil, peanut oil, corn oil, Neat's foot oil and the like. A particularly preferred acid is oleic acid.

[051] The fatty acid monoester of glycerol is preferred, however, mixtures of mono- and diesters may be used. Preferably any mixture of mono- and diester contains at least 40% of the monoester. Typically these mixtures of mono- and diesters of glycerol contain from 40 to 60 percent by weight of the monoester. For example, commercial glycerol monooleate contains a mixture of from 45% to 55% by weight monoester and from 55% to 45% diester. However, higher mono ester can be achieved by distilling the glycerol monoester, diester, triester mixture using conventional distillation techniques, with the monoester portion of the distillate product recovered. This can result in a product which is essentially all monoester. Thus, the esters used in the fuel compositions of this invention may be all monoesters, or a mixture of mono-

and diesters in which at least 75 mole percent, preferably at least 90 mole percent, of the mixture is the monoester.

Fuel Compositions

[052] The compounds of the present disclosure may be useful as additives in hydrocarbon fuels to prevent or reduce engine knock or pre-ignition events in spark-ignited internal combustion engines.

[053] The compounds of the present disclosure may be formulated as a concentrate using an inert stable oleophilic (i.e., soluble in hydrocarbon fuel) organic solvent boiling in a range of 65°C to 205°C. An aliphatic or an aromatic hydrocarbon solvent may be used, such as benzene, toluene, xylene, or higher-boiling aromatics or aromatic thinners. Aliphatic alcohols containing 2 to 8 carbon atoms, such as ethanol, isopropanol, methyl isobutyl carbinol, *n*-butanol and the like, in combination with the hydrocarbon solvents are also suitable for use with the present additives. In the concentrate, the amount of the additive may range from 10 to 70 wt % (e.g., 20 to 40 wt %).

[054] In gasoline fuels, other well-known additives can be employed including oxygenates (e.g., ethanol, methyl *tert*-butyl ether), other anti-knock agents, and detergents/dispersants (e.g., hydrocarbyl amines, hydrocarbyl poly(oxyalkylene) amines, succinimides, Mannich reaction products, aromatic esters of polyalkylphenoxyalkanols, or polyalkylphenoxyaminoalkanes). Additionally, friction modifiers, antioxidants, metal deactivators and demulsifiers may be present.

[055] In diesel fuels, other well-known additives can be employed, such as pour point depressants, flow improvers, cetane improvers, and the like.

[056] A fuel-soluble, non-volatile carrier fluid or oil may also be used with compounds of this disclosure. The carrier fluid is a chemically inert hydrocarbon-soluble liquid vehicle which substantially increases the non-volatile residue (NVR), or solvent-free liquid fraction of the fuel additive composition while not overwhelmingly contributing to octane requirement increase. The carrier fluid may be a natural or synthetic oil, such as mineral oil, refined petroleum oils, synthetic polyalkanes and

alkenes, including hydrogenated and unhydrogenated polyalphaolefins, synthetic polyoxyalkylene-derived oils, such as those described in U.S. Patent Nos. 3,756,793; 4,191,537; and 5,004,478; and in European Patent Appl. Pub. Nos. 356,726 and 382,159.

[057] The carrier fluids may be employed in amounts ranging from 35 to 5000 ppm by weight of the hydrocarbon fuel (e.g., 50 to 3000 ppm of the fuel). When employed in a fuel concentrate, carrier fluids may be present in amounts ranging from 20 to 60 wt % (e.g., 30 to 50 wt %).

[058] The following non-limiting examples have been provided to illustrate one or more aspects of the present invention.

Example 1

Fuel Consumption Test

[059] Additives were added to fuel to make fuel composition samples. The samples are summarized in Table 1 below. Table 2 summarizes the various conditions of the fuel consumption test.

Table 1

Fuel Sample #	Composition
1	Diethanolisostearamide (DEIS)
2	Glycerol Monooleate (GMO)
3	DBU Oleate
4	AHPD salt
5	AHPD
6	Unadditized base fuel
7	ACAC + GMO

Table 2

Engine RPM (rpm)	Engine Pressure (bar)
1100	3 (cold)
2500	6
3000	14
1100	3
3000	10
2000	8
2000	2

[060] Figure 1 shows the results of the fuel consumption test on the fuel samples at the various engine conditions. The engine rpm ranges from 1100 to 3000 rpm while the pressure ranges from 2 to 14 bars.