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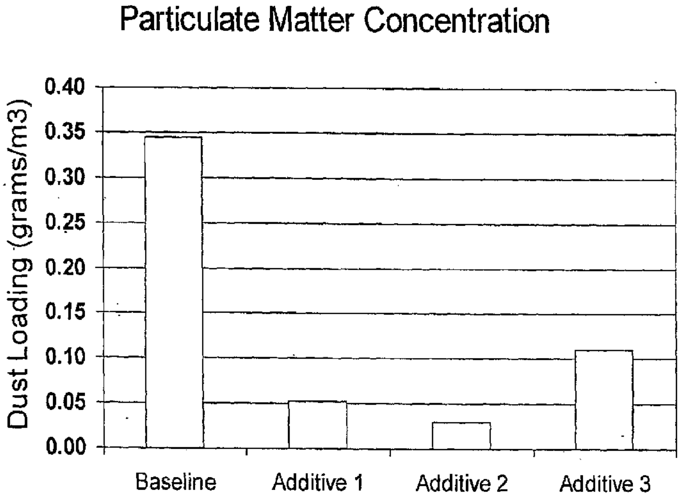
(54) **Title:** RESIDUAL FUEL OIL ADDITIVE



(57) **Abstract:** Fuel additives are disclosed for high-asphaltene carbonaceous fuels such as residual fuel oil or coal. Such additives provide improved combustion characteristics. Such improved combustion characteristics include one or both of improved efficiency and decreased emissions of pollutants. In particular, the fuel additives include an extract from a plant such as fescue, alfeque, or alfalfa, and optionally, an organometallic compound. The use of a fuel additive including both a plant extract and an organometallic compound is particularly useful in improving the combustion characteristics of fuels with particularly high asphaltene content.

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RESIDUAL FUEL OIL ADDITIVE

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of Provisional Application No. 60/753,318, filed December 21, 2005, the entire disclosure of which is incorporated by reference.

TECHNICAL FIELD

[0002] The invention pertains to fuel additives for carbonaceous fuels having high asphaltene content such as residual fuel oil and coal. Benefits from the use of such fuel additives may include one or more of reduced particulate matter emissions, reduced nitrogen oxide emissions, and improved combustion efficiency.

BACKGROUND OF THE INVENTION

[0003] Carbonaceous fuels with high asphaltene content such as residual fuel oil and coal tend to liberate large amounts of energy on combustion, and therefore, find utility in applications where a low cost, high energy fuel is desired. However, such high-asphaltene carbonaceous fuels generally burn with less efficiency than other hydrocarbon fuels, and may often contain quantities of undesirable compounds that limit combustion and result in elevated levels of pollutants.

[0004] Residual fuel oils (also referred to as “resid” or “resid fuel”) are generally the low grade products that remains after the distillation of lighter petroleum products which may include gasoline, jet fuel, diesel fuel, No. 4 fuel oil, and No. 5 light or heavy fuel oil. Examples of residual fuel oils include No. 6 fuel oil and Bunker C fuel oil.

[0005] The compounds referred to as "asphaltenes" generally include polynuclear aromatics and/or polycyclic materials. While certain parts of the world such as North America tend to have specifications which limit the amount of asphaltenes in fuels such as residual fuel oils, such fuels still have relatively high levels of asphaltenes compared to other, lighter hydrocarbon fuels. For example, in the United States, specifications limit the asphaltene content of residual fuel oil to less than about 8 wt.%. However, in other parts of the world, asphaltene specifications tend to be either non-existent, or significantly higher than those in North America. Therefore, residual fuel oils in other parts of the world may have asphaltene contents of 10 wt.% or higher. As a fairly heavy carbonaceous fuel, coal also tends to have high concentrations of ring structures which may include anthracene and phenanthrene which for purposes of this specification are to be included as "asphaltenes." It should be noted that as coal becomes "older," more of such rings form and become interconnected such that coal can also be considered a high-asphaltene carbonaceous fuel.

For purposes of this specification, the term "high-asphaltene carbonaceous fuel" is intended to broadly encompass carbonaceous fuels which have asphaltene content of at least 4 wt%.

[0006] Examples of the pollutants that can result from the combustion of high-asphaltene carbonaceous fuels include ozone, particulate matter (PM), carbon monoxide, nitrogen oxides (NO_x), sulfur dioxide, polynuclear aromatic compounds, and soluble organic fractions. In the United States, numerous state and national agencies have or are adopting ambient air quality standards which may require reduced emissions from the combustion of high-asphaltene carbonaceous fuels. Among the users of resid oils are power plants and ocean-going ships. In Southern California, for example, emissions from ships entering the port of Los Angeles are considered to be a major cause of regional air pollution.

[0007] Considerable effort has been expended by petroleum refiners to formulate fuels that reduce emissions. The most common approach to formulating compliant fuels involves adjusting refinery processes so as to produce a fuel meeting the specifications set forth by appropriate government agencies. However, such an approach is difficult for residual fuels, and the drawbacks to such an approach include high costs in reconfiguring refinery processes, and possible negative effects on the quantity or quality of other refinery products.

SUMMARY OF THE INVENTION

[0008] Embodiments of the present invention include systems, methods, and compositions which may provide improved combustion characteristics of high-asphaltene carbonaceous fuels. Examples of the combustion characteristics which may be improved by embodiments of the invention include one or both of increased combustion efficiency, and reduced pollutant discharge. Examples of the pollutants which may be reduced include one or more of ozone, particulate matter (PM), carbon monoxide, nitrogen oxides (NO_x), sulfur dioxide, polynuclear aromatic compounds, and soluble organic fractions.

[0009] In some embodiments, a fuel additive is provided comprising a plant extract. In this specification, the term "plant extract" is intended to broadly encompass extracts of all types of plants, excluding the roots and bark, and even includes plants such as algae. Suitable plant extracts are extracts from green and other colored plants as such plants tend to have high concentrations of desirable extracts. However, even white and light colored plants include such extracts, though at lower concentrations. Particularly suitable extracts are from green and other dark leafy plants such as those from the *Leguminosae* family which includes fescue, alfeque, and alfalfa.

[0010] In a preferred embodiment, the plant extract is combined with an organometallic material. The inclusion of an organometallic compound is especially useful for treating fuels having particularly high asphaltene contents in the range of 8 wt. % or higher. Examples of organometallic materials are hydrocarbon-soluble organometallic compounds that include a metal selected from the first and second row transition metals. One metal of particular interest is iron, and particularly suitable organometallic materials include iron pentacarbonyl, iron naphthenate, ferrocene, and combinations. The fuel additive may optionally include an oil-soluble carrier. Examples of suitable oil-soluble carriers include hydrocarbons such as toluene, aromatic blends, naphthas, gasoline, diesel fuel, jet fuel, and mixtures thereof. In one embodiment, the oil soluble carrier is non-oxygenated.

[0011] In certain embodiments, the fuel additive may include other optional ingredients. Such optional ingredients may include one or more of an oxygen carrier, a stability aid, a lubricity aid, an anti-oxidant, and a combustion improver. Meadowfoam oil may be used as a stability aid, an anti-oxidant, and a lubricity aid. Suitable oxygen carriers include carotenoids. Examples of antioxidants include 1,2-dihydroquinolines, and in particular, 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline. Examples of combustion improvers include compounds known as cetane improvers or ignition accelerators. Examples of combustion improvers include alkyl nitrates such as 2-ethylhexyl nitrate.

[0012] In another embodiment of the present invention, a method for improving the combustion characteristics of a high-asphaltene carbonaceous fuel comprises adding a fuel additive as described above to a high-asphaltene carbonaceous fuel prior to or during combustion.

[0013] In another embodiment of the present invention, an additized high-asphaltene carbonaceous fuel is provided which comprises a high-asphaltene carbonaceous fuel and a fuel additive as described above.

[0014] In still another embodiment of the invention, a method for preparing a fuel additive comprises mixing a plant extract with an oil-soluble carrier and one or more of an organometallic material, an oxygen carrier, a stability aid, a lubricity aid, an anti-oxidant, and a combustion improver. In another embodiment of the invention, the fuel additive is prepared in an oxygen-free or reduced-oxygen atmosphere, and optionally may include the step of excluding sources of UV radiation during the preparation. In still another embodiment, non-oxidized oil-soluble carriers and non-oxidized oxygen carriers are used.

[0015] The plant extract used in various embodiments of the invention may be obtained by solvent extraction from whole plants using hydrocarbon-soluble solvents. Polar or nonpolar hydrocarbon-soluble solvents may be used for the extraction. The extract resulting from the extraction process is a crude material containing over 300 individual compounds. In one embodiment, the extract has a paste- or mud-like consistency that may be described as a solid or semi-solid, rather than a liquid. Such extracts typically contain chlorophyll A and chlorophyll B with a higher concentration of chlorophyll A over chlorophyll B. The color of such an extract is generally a deep black-green with some degree of fluorescence. Such an extract may be recovered from most plants though green and darker leafy plants tend to have higher concentrations. Extracts from plants from the *Leguminosae* family are suitable. While such a solid or semi-solid form is generally considered to be preferred for most embodiments, in other embodiments, a liquid or other form may be suitable, and may even be preferred. Furthermore, synthetic materials, for example synthetic carotenoids, chlorophylls, or xanthopylls, may be used instead of or in addition to natural plant extracts.

[0016] The foregoing has outlined rather broadly the features and technical advantages of the present invention in order that the detailed description of the invention that follows may be better understood. Additional features and advantages of the invention will be described hereinafter which form the subject of the claims of the invention. It should be appreciated by those skilled in the art that the conception and specific embodiments disclosed may be readily utilized as a basis for modifying or designing other structures for carrying out the same purposes of the present invention. It should also be realized by those skilled in the art that such equivalent constructions do not depart from the spirit and scope of the invention as set forth in the appended claims. The novel features which are believed to be characteristic of the invention, both as to its organization and method of operation, together with further objects and advantages will be better understood from the following description when considered in connection with the accompanying figures. It is to be expressly understood, however, that each of the figures is provided for the purpose of illustration and description only and is not intended as a definition of the limits of the present invention.

BRIEF DESCRIPTION OF THE DRAWINGS

[0017] For a more complete understanding of the present invention, reference is now made to the following descriptions taken in conjunction with the accompanying drawing, in which:

[0018] FIG. 1 is a plot of NO_x emissions measured at the furnace exit for the various fuel additives used in the EERC Test;

[0019] FIG. 2 is a plot of NO_x emissions measured at the baghouse for the various fuel additives used in the EERC Test;

[0020] FIG. 3 is a plot of dust loading for the EERC Test;

[0021] FIG. 4 is a plot of heat flux divided by fuel firing rate versus excess air for the EERC Test; and

[0022] FIG. 5 is a plot of feed rate versus temperature for the EERC Test.

DETAILED DESCRIPTION

[0023] As used in this specification, the term "β-carotene mixture" is defined as a mixture of from about 89 to about 98% trans β-carotene with the remainder being from about 2 to 11% of various cis β-carotene isomers or other poly-unsaturated conjugated hydrocarbons.

An example of such a β-carotene mixture is ISOMIXTENE®, a product sold by DSM Nutritional Products, Inc. of Parsippany, New Jersey.

[0024] Embodiments of the present invention are directed to systems, methods, and compositions which improve the combustion characteristics of high-asphaltene carbonaceous fuels. Examples of the combustion characteristics which may be improved include increased combustion efficiency, and reduced emissions of one or more pollutants such as ozone, particulate matter (PM), carbon monoxide, nitrogen oxides (NO_x), sulfur dioxide, polynuclear aromatic compounds, and soluble organic fractions.

[0025] In one embodiment, a fuel additive comprises a plant extract. Suitable plant extracts include extracts from green leafy plant material. Particularly useful plant extracts are extracts from plants of the *Leguminosae* family which may include fescue extract, alfeque extract, alfalfa extract, and combinations thereof. The plant extract may be provided in an amount such that the high-asphaltene carbonaceous fuel to be treated includes a plant extract concentration by weight in the range of about 0.5 ppm to about 10,000 ppm, preferably from about 200 ppm to about 2000 ppm, and more preferably at about 800 ppm. Without being bound by theory, it is believed that the oxygen-gathering properties of such plant extracts provide the beneficial improvements to the combustion of high-asphaltene carbonaceous fuels such as residual fuel oil and coal.

[0026] The plant extracts may be obtained using extraction methods well known to those of skill in the art. Solvent extraction methods using polar or nonpolar hydrocarbon-soluble solvents are generally preferred. Any suitable extraction solvent may be used which is capable of separating the suitable fractions from the plant material. Suitable nonpolar solvents include cyclic, straight chain, and branched-chain alkanes containing from about 5 or fewer to 12 or more carbon atoms. Specific examples of acyclic alkane solvents include pentane, hexane, heptane, octane, nonane, decane, mixed hexanes, mixed heptanes, mixed octanes, isooctane, and the like. Examples of cycloalkane solvents include cyclopentane, cyclohexane, cycloheptane, cyclooctane, methylcyclohexane, and the like. Alkenes such as hexenes, heptenes, octenes, nonenes, and decenes are also suitable for use, as are aromatic hydrocarbons such as benzene, toluene, and xylene. Halogenated hydrocarbons such as chlorobenzene, dichlorobenzene, trichlorobenzene, methylene chloride, chloroform, carbon tetrachloride, perchloroethylene, trichloroethylene, trichloroethane, and trichlorotrifluoroethane may also be used. Generally preferred nonpolar solvents are C_6 to C_{12} alkanes, particularly n-hexane.

[0027] Suitable polar solvents may include, but are not limited to, acetone, methyl ethyl ketone, other ketones, methanol, ethanol, other alcohols, tetrahydrofuran, methylene chloride, chloroform, or any other suitable polar solvent.

[0028] Hexane extraction is a commonly used technique for extracting oil from plant material. It is a highly efficient extraction method that extracts virtually all oil-soluble fractions from the plant material. In a typical hexane extraction, the plant material is comminuted. Grasses and leafy plants may be chopped into small pieces while seeds are typically ground or flaked. The plant material may be pelletized to pellets of ½ to ¾ inch. The plant material is typically exposed to hexane at an elevated temperature. The hexane, a highly flammable, colorless, volatile solvent that dissolves out the oil, typically leaves only a few weight percent of the oil in the residual plant material. The oil and solvent mixture may be heated to about or above 100°C to remove most of the hexane, and may then be distilled to remove all traces of hexane. Alternatively, hexane may be removed by evaporation at reduced pressure. The resulting plant extract is suitable for use in producing the fuel additives of the present invention.

[0029] Other extraction processes include supercritical fluid extraction, typically with carbon dioxide, but other gases such as helium, argon, xenon, and nitrogen may also be used as solvents in supercritical fluid extraction methods.

[0030] Still another useful extraction process is mechanical pressing, also known as expeller pressing, which removes oil through the use of continuously driven screws that crush the seed or other oil-bearing material into a pulp from which the oil is expressed. Friction created in the process can generate temperatures between about 50°C and 90°C, or external heat may be supplied. Cold pressing generally refers to mechanical pressing conducted at a temperature of 40°C or less with no external heat applied. The yield of oil extract that may be obtained from a plant material may depend upon any number of factors, but primarily upon the oil content of the plant material. For example, a typical oil content of vetch (hexane extraction, dry basis) is approximately 4 to 5 wt. %, while that for barley is approximately 6 to 7.5 wt. %, and that for alfalfa is approximately 2 to 4.2 wt.%.

[0031] Plant oil extracts for use in edible items or cosmetics typically undergo additional processing steps to remove impurities that may affect the appearance, shelf life, taste, and the like, to yield a more refined product. The impurities include may include phospholipids, mucilaginous gums, free fatty acids, color pigments and fine plant particles. Different methods are used to remove these by-products including water precipitation or precipitation with aqueous solutions of organic acids. Color compounds are typically removed by bleaching, wherein the oil is typically passed through an absorbent such as diatomaceous clay. Deodorization may also be conducted, which typically involves the use of steam distillation. While the extracts used as fuel additives in the present invention may include such additional processing steps, such additional steps are generally unnecessary.

[0032] The fuel additive may optionally include an organometallic compound. Suitable organometallic compounds are hydrocarbon-soluble organometallic compounds that include a metal selected from the first and second row transition metals particularly suitable organometallic compounds include iron pentacarbonyl, iron naphthenate, ferrocene, and combinations. The inclusion of an organometallic compound is believed to be particularly useful in improving the combustion characteristics of fuels with particularly high asphaltene content such as residual fuel oils used in areas of the world other than North America. The organometallic compound may be provided in an amount such that the fuel to be treated includes a concentration by weight of organometallic compound in the range of about 0.5 ppm to about 10,000 ppm as metal, preferably from about 200 ppm to about 2000 ppm as metal, and more preferably at about 800 ppm as metal. Without being bound by theory, it is believed that the inclusion of an organometallic compound provides a catalytic effect to the reactions promoted by the plant extract material.

[0033] The fuel additive may further comprise meadowfoam oil. Meadowfoam oil has a number of useful properties, and can function as an oxygen carrier, a stability aid, and an anti-oxidant. Because the plant extracts used in the fuel additives of the present invention have oxygen-gathering properties, and therefore, can be unstable, the inclusion of a material such as meadowfoam oil can help to maintaining the stability of the plant extracts and prevent their oxidation.

[0034] The composition may further optionally include at least one carotene which may be provided in the form of a β-carotene mixture such as ISOMIXTENE®. Although carotenoids such as β-carotene mixtures are disclosed, other molecules having extended pi or double bonded structures of from about 2 to 11 or more conjugated double bonds are also believed to similarly provide improved combustion characteristics for resid or other hydrocarbon fuels when used as additives for such fuels. The moieties of such molecules including the double bond structures can be terminated by at least one end group further comprising an aromatic, cyclic, or branched 5 to 8 carbon moiety that is saturated or unsaturated. Examples include cyclo-pentane, cyclo-pentene, cyclo-hexane, cyclo-hexene, cyclo-heptane, cyclo-heptene, isopentane or isopentene. Aromatic structures are considered as extended pi structures also. The unsaturated/aromatic portions and the end groups can additionally include various other substituents such as hydroxyl groups, keto groups, alkyl groups, alkenyl groups and combinations. Additionally, the additive molecules can comprise from 12 to about 40 or 50 carbon atoms. Such molecules are found in mixtures of synthetic carotene precursors. Such additives may be obtained from natural or synthetic sources.

[0035] Furthermore, lycopene is another example of a suitable carotene. Other suitable carotenoids and carotene precursors are disclosed in German patent 954,247, issued in 1956 and incorporated by reference.

[0036] If the fuel additive comprises a carotene, it may further comprise an antioxidant. Suitable antioxidants include alkyl phenols such as 2-tert-butylphenol, 2,6-di-tert-butylphenol, 2-tert-butyl-4-n-butylphenol-, 2,4,6-tri-tert-butylphenol, 2,6-di-tert-butyl-4-n-butylphenol, and mixtures thereof. Such antioxidants are suited for use as stabilizers for middle distillate fuels. Other antioxidants include hindered phenolic antioxidants such as 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-4-hydroxyphenyl) 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; tris(3,5-di-t-butyl-4-hydroxybenzyl)isocyanurate, pentaerythritol co-esters derived from pentaerythritol, (3-alkyl-4-hydroxyphenyl)-alkanoic acids and alkylthioalkanoic acids or lower alkyl esters of such acids, and combinations thereof. Such stabilizers are useful with organic material normally susceptible to oxidative and/or thermal deterioration. Also useful are the reaction product of malonic acid, dodecyl aldehyde and tallowamine, hindered phenyl phosphates, hindered piperidine carboxylic acids and metal salts thereof; acylated derivatives of 2,6-dihydroxy-9-azabicyclo[3.3.1]nonane; bicyclic hindered amines; sulfur containing derivatives of dialkyl-4-hydroxyphenyltriazine, bicyclic hindered amino acids and metal salts thereof, trialkyl substituted hydroxybenzyl malonates, hindered piperidine carboxylic acids and metal salts thereof, pyrrolidine dicarboxylic acids and esters, metal salts of N,N-disubstituted .beta.-alanines, hydrocarbyl thioalkylene phosphates, hydroxybenzyl thioalkylene phosphates, and the like.

[0037] Specific antioxidants useful in the present invention are the quinoline or hydro quinoline compounds such as 1,2 dihydro quinoline compounds. More particularly, 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline, commonly referred to as ethoxyquin, may be used as an antioxidant. Ethoxyquin is sold under the trademark SANTOQUIN® by Novus International Inc. of St. Louis, Missouri, and is widely used as an antioxidant for animal feed and forage.

[0038] The fuel additives of the present invention may also contain a combustion improver such as a cetane improver or ignition accelerator. Suitable combustion improvers are organic nitrate materials. Preferred organic nitrates are substituted or unsubstituted alkyl or cycloalkyl nitrates having up to about 10 carbon atoms, and preferably from 2 to 10 carbon atoms. The alkyl group can be either linear or branched. Specific examples of suitable nitrate compounds include methyl nitrate, ethyl nitrate, n-propyl nitrate, isopropyl nitrate, allyl nitrate, n-butyl nitrate, isobutyl nitrate, sec-butyl nitrate, tert-butyl nitrate, n-amyl nitrate, isoamyl nitrate, 2-amyl nitrate, 3-amyl nitrate, tert-amyl nitrate, n-hexyl nitrate, 2-ethylhexyl nitrate, n-heptyl nitrate, sec-heptyl nitrate, n-octyl nitrate,, sec-octyl nitrate, n-nonyl nitrate, n-decyl nitrate, n-dodecyl nitrate, cyclopentylnitrate, cyclohexylnitrate, methylcyclohexyl nitrate, isopropylcyclohexyl nitrate, and the esters of alkoxy substituted aliphatic alcohols, such as 1-methoxypropyl-2-nitrate, 1-ethoxpropyl-2 nitrate, 1-isopropoxybutyl nitrate, 1-ethoxylbutyl nitrate and the like. Preferred alkyl nitrates are ethyl nitrate, propyl nitrate, amyl nitrates, and hexyl nitrates. Other preferred alkyl nitrates are mixtures of primary amyl nitrates or primary hexyl nitrates. By "primary" it is meant that the nitrate functional group is attached to a CH_2 group of the amyl or hexyl group. Examples of primary hexyl nitrates include n-hexyl nitrate, 2-ethylhexyl nitrate, 4-methyl-n-pentyl nitrate, and the like. Preparation of the nitrate esters can be accomplished by any of the commonly used methods, such as by esterification of the appropriate alcohol, or reaction of a suitable alkyl halide with silver nitrate. These additives can be present the same or different amounts as the other components of the fuel additive

[0039] The fuel additives may further include a diluent or solvent carrier. Such a carrier is useful because, in general, low concentrations of the particular components of the fuel additive are effective in achieving desirable results, and therefore, the use of a carrier simplifies the addition of the fuel additive. The use of a carrier can further help to maintain the components in solution, and can help to prevent oxidation of the components.

[0040] Suitable solvents for use as the carrier include one or more of an aromatic hydrocarbon such as toluene or xylene, or other hydrocarbons such as gasoline, jet fuel, or diesel fuel. In one embodiment, a mixed aromatic solvent comprising various xylene isomers is used. Examples of such solvents include those commercially available in North America from ExxonMobil Chemical and sold under the names AROMATIC 100 FLUID and AROMATIC 150 FLUID. In one embodiment, a mixture of AROMATIC 100 FLUID AND AROMATIC 150 FLUID is used.

[0041] When blending the particular components of the fuel additive, it may be useful to prepare the fuel additive in an oxygen free or low oxygen atmosphere to prevent oxidation of the fuel additive components. Optionally, the components may be blended under conditions in which sources of UV radiation are excluded to further prevent degradation of the components.

[0042] In those embodiments where the fuel additive includes a plant extract such as fescue extract, alfeque extract, or alfalfa extract, meadowfoam oil, and a carotene, the weight ratio of plant extract to carotene may be from about 50:1 to about 20:1, and preferably is from about 24:1 to about 10:1. The ratio of grams of plant extract to milliliters of meadowfoam oil may be from about 12:1 to about 20:1, and preferably is from about 6:1 to about 10:1. The ratio of milliliters meadowfoam oil to grams of carotene may be from about 12:1 to about 20:1, and preferably is from about 6:1 to about 1:1.

[0043] In those embodiments where the fuel additive includes a carotene and an antioxidant, the ratio of carotene to antioxidant may be from about 20:1 to about 1:1, preferably is from about 15:1 to about 5:1, and more preferably is about 10:1.

[0044] In another embodiment of the invention, where the fuel additive includes plant extract and meadowfoam oil, the two may be provided in a weight ratio from about 1:100 to about 100:1. In an embodiment of the invention, the concentration of plant extract in the total fuel additive composition may be from about 0.06 weight % to about 6 weight %, and preferably is from about 0.12 weight % to about 3 weight %. The concentration of meadowfoam oil may range from about 0.05 weight % to about 5 weight % of the total fuel additive composition, and preferably is about 0.5 weight % of the total fuel additive composition.

[0045] Such fuel additives may be blended into high-asphaltene carbonaceous fuels such that the plant extract and organometallic material are present in the fuel in the concentrations set forth above.

[0046] In embodiments in which the fuel additive includes a plant extract, a non-oxidized carotene, an antioxidant, and meadowfoam oil, certain factors may be useful in determining appropriate ratios for the components. Such factors may include the elevation at which the fuel is to be combusted, the type of engine or device using the fuel, and the particular fuel properties. Examples of different types of engines or devices include two-cycle diesel engines and stationary boilers. Examples of relevant fuel properties include sulfur content, mercaptan content, olefin content, aromatic content and asphaltene content. For example, if a fuel has a high sulfur content of 1 wt. % or more, or a high aromatics content of 25 wt. % or more, the ratios may be adjusted such as to provide additional plant extract or additional non-oxidized carotene.

[0047] According to another embodiment of the invention, an additized fuel is provided in which a fuel additive as set forth above is blended with a high-asphaltene carbonaceous fuel. Formulated fuel compositions according to embodiments of the invention can further contain other known additives such as detergents, antioxidants, demulsifiers, corrosion inhibitors, metal deactivators, diluents, cold flow improvers, and thermal stabilizers.

[0048] According to another embodiment of the invention, a method for improving combustion characteristics of a high-asphaltene carbonaceous fuel comprises the step of adding such a fuel additive to a high-asphaltene carbonaceous fuel prior to or during combustion.

[0049] Fuel additives of the present invention may be introduced into residual fuel oil in a number of different ways. For example, the residual fuel oil to be combusted may be pre-mixed to include the fuel additive. In another example, the fuel additive is injected into a residual fuel oil stream being fed to a burner or other combustion device. In such an embodiment, the fuel additive may be injected using a metered injection system. Such a metered injection system may optionally be controlled by a computer system that can optimize the flow of any or all of the components to the combustion device to optimize its operation.

[0050] For coal, such fuel additives can similarly be added in a number of different ways. For example, the fuel additive may be sprayed over the coal prior to combustion. Alternatively, the fuel additive may be pumped or sprayed into the coal burner along with the coal using a metered injection system as described above.

EERC Laboratory Testing

[0051] Test runs were conducted at the EERC Laboratory in Grand Forks, North Dakota. Six drums of residual fuel oil were used in the tests. The residual fuel oil was supplied by Sun Coast Resources in Houston, Texas. The properties of the residual fuel oil used are set forth in Table 1. It has a moderate sulfur content of about 2.63%, with a very high heating value of 44.5 MJ/kg at a moisture content of 2.40%. The Karl Fischer water content was determined to be 0.21%. The volatile content of the sample was determined to be 89.30%, with fixed carbon present at the 8.29% level. The theoretical emission limit of sulfur dioxide was determined to be 1714 ppm at a flue gas oxygen concentration of 2.0%. This equates to a 1.18 kg/MJ emission rate for the sulfur dioxide (SO_2). The residual fuel oil had a specific gravity of 0.9952, and the amount of sediment was determined to be 0.05%. Table 1 also provides the proximate, ultimate, and heating value analyses for the residual fuel oil tested along with the theoretical emission limit of sulfur.

Table 1. As-fired Residual Fuel Oil Analyses (standard ASTM* analyses)

Test Number	AF-CTS-745 & 746	
Fuel Description Sample Number	Residual Fuel Oil 05-0165	
	As-Fired	H_2O-free
Proximate Analysis, %		
Moisture	2.40	--
Volatile Matter	89.30	91.48
Fixed Carbon	8.29	8.51
Ash	0.01	0.01

Ultimate Analysis, %		
Hydrogen	10.48	10.46
Carbon	83.41	85.44
Nitrogen	0.86	0.88
Sulfur	2.63	2.69
Oxygen	2.62	0.52
Ash	0.01	0.01
Heating Value, MJ/kg	44.25	45.33
Maximum SO_2, ppm @ 3.5% O_2	1714	
g/MJ	5.74	
Specific Gravity @ 60°F	0.9952	
Karl Fischer Water, %	0.21	
Sediment, %	0.05	

*American Society for Testing and Materials

[0052] The residual fuel oil was stored cold prior to testing. Barrel heaters were used to heat the residual fuel oil to 121°C prior to transferring it to the feed hopper situated above the pump. A barrel heater was strapped to the tank of the feed hopper to keep the residual fuel oil hot during testing, averaging between 113° and 118°C for use in the test periods shown here. Although the oil appeared to be rather viscous at this temperature, a homogeneous phase was maintained so that a readily controllable feed rate to the combustor was achieved for all test periods.

[0053] The test apparatus at the EERC facility includes a furnace with a capacity of approximately 19 kg/hr (845 MJ/hr) of residual fuel oil. The combustion chamber is 0.76 meters in diameter, 2.44 meters high, and refractory-lined for combustion testing of various types of fuels. The furnace diameter may be reduced to 0.66 meters to elevate the temperature entering the convective pass. Furnace exit gas temperatures (FEGTs) as high as 1400 °C have been achieved during combustion testing in this mode. However, most tests are performed using the standard configuration (0.76 meter inside diameter), with the FEGT maintained between 1100 °C and 1200 °C though the FEGT is typically raised to between 1250 °C and 1300 °C for the combustion of residual fuel oil. Two Type S thermocouples, located at the top of the combustion chamber, are used to monitor the FEGT. They are situated 180° apart at the midpoint of the transition from vertical to horizontal flow. Excess air levels are controlled manually by adjusting valves on the primary and secondary air streams. The typical distribution is 15% primary and 85% secondary to achieve a typical excess air level of 20%.

[0054] When firing liquid fuels such as residual fuel oil, a pump is used to convey the fuel through a dual-fluid atomizer into the combustion chamber. Air or steam is commonly used as the atomizing fluid. Combustion air is preheated by an electric air heater. Heated secondary air is introduced through an adjustable swirl burner. Flue gas passes out of the furnace into a 10-inch-square duct that is also refractory-lined. A vertical probe bank located in the duct is designed to simulate superheated surfaces in a commercial boiler. After leaving the probe duct, the flue gas passes through a series of water-cooled, refractory-lined heat exchangers and a series of air-cooled heat exchangers before being discharged through either an electrostatic precipitator (ESP) or a baghouse (BH) for particulate removal.

[0055] At the EERC facility, flame stability is assessed by observation of the flame and its relation to the burner quarl as a function of secondary air swirl and operating conditions at full load and under turndown conditions. An International Flame Research Foundation-(IFRF)-type adjustable secondary air swirl generator uses primary and secondary air at approximately 15% and 85% of the total air, respectively, to adjust swirl between 0 and a maximum of 1.9. Swirl is defined as the ratio of the radial (tangential) momentum to axial momentum imparted to the secondary air by movable blocks internal to the burner and is used to set up an internal recirculation zone (IRZ) within the flame that allows greater mixing of combustion air and fuel. Swirl is imparted by moving blocks to set up alternate paths of radial flow and tangential flow to create a spin on the secondary air stream that increases the turbulence in the near-burner zone.

[0056] At the fully open position of the swirl block, the secondary air passes through the swirl burner unaffected, and the momentum of this stream has only an axial component such that the air enters the combustion chamber as a jet. As the angle of the blocks changes, the air begins to spin or "swirl" and the radial component of the momentum is established, creating the IRZ in the near burner region. It is the ratio of this radial component of the momentum to the axial component that establishes the quantity defined as swirl.

[0057] The adjustable-swirl burner used by the EERC during flame stability testing consists of two annular plates and two series of interlocking wedge-shaped blocks, each attached to one of the plates. The two sets of blocks can form alternate radial and tangential flow channels, such that the air flow splits into an equal number of radial and tangential streams which combine further downstream into one swirling flow. By simply rotating the movable plate, radial channels are progressively closed and tangential channels opened so that the resulting flux of angular momentum increases continuously, between zero and a maximum value. This maximum swirl setting depends on the total air flow rate and the geometry of the swirl generator. Swirl can be calculated from the dimensions of the movable blocks (the ratio of the tangential and radial openings of the blocks) or from the measurement of the velocity of the air stream (obtaining both radial and axial components).

[0058] Secondary air swirl is used to stabilize the flame. In the absence of swirl, loss of flame may result, increasing the risk of dust explosion. As swirl is applied to the combustion air, fuel droplets are entrained in the IRZ, increasing the heating rate of the particles and leading to the increased release of volatiles and char combustion. The flame becomes more compact and intense as swirl is increased to an optimum level, which is characterized in the EERC test facility as the point at which the flame makes contact with the burner quarl. Increasing swirl beyond this level can pull the flame into the burner region, unnecessarily exposing metal burner components to the intense heat of the flame and possible combustion in the coal pipe. Adjustments to the swirl setting were made manually by moving a lever arm attached to the movable block assembly. The position of the blocks was noted on a linear scale.

[0059] Increasing swirl to provide flame stability and increased carbon conversion can also affect the formation of NO_x. The high flame temperatures and increased fuel-air mixing associated with increased swirl create an ideal situation under which NO_x may form. In full-scale burners with adjustable vanes, swirl is often increased to reach the optimum condition for carbon conversion, and then decreased slightly to reduce the production of NO_x.

[0060] The general test method at the EERC facility sets the burner at its maximum level of swirl and monitors system parameters such as fuel feed rate, excess air, gaseous emissions such as O_2, CO_2, CO, SO_2, and NO_x, combustor static, and air flow rates. Photographs of the flame and burner zone were taken through a sight port in the furnace just above the burner cone using standard 35-mm film. Flame temperature was also measured using a high-velocity thermocouple (HVT) at a set location in the furnace, and heat flux was monitored using a baseline heat-flux probe at the same location. An ash sample was collected at each swirl setting to establish carbon burnout. The swirl setting was then reduced until the flame was visually observed to lift off the burner quarl. At this point, the flame was characterized as unstable under full load conditions which are between 633 and 686 MJ/hr firing rate. Photographs were again taken to record the flame at this setting, temperature and heat flux measurements were taken, and an ash sample was taken once again. Once flame liftoff was established, the optimum swirl setting was located by visual observation of the flame, and measurements were recorded once again.

[0061] Flame stability under turndown conditions is characterized by firing the test fuel at a reduced load, typically one-half to three-quarters of the full load rate, maintaining the same primary air flow, and adjusting the secondary air flow to meet excess air requirements. The procedure described above was used to establish flame stability at reduced load.

[0062] The CTF utilizes two banks of Rosemount NGA gas analyzers to monitor O_2, CO, CO_2, and NO_x. Sulfur dioxide (SO_2) is monitored by analyzers manufactured by Ametek. The analyzers are typically located at the furnace exit and the particulate control device exit.

The gas analyses are reported on a dry basis. Baldwin Environmental manufactures the flue gas conditioners used to remove water vapor from each gas sample. The flue gas constituents are constantly monitored and recorded by the CTF's data acquisition system.

[0063] One of the probes used to characterize flame shape and intensity is the baseline heat-flux probe. The probe uses water to pick up heat from a 2.5 cm-thick stainless steel tip that is inserted into a port in the sidewall of the radiant zone so that its surface is flush with the inner wall of the combustion chamber. The water flow rate is measured by turbine flow meters and the temperature of the water is measured by Type K thermocouples in the inlet and exit water streams. Two thermocouples embedded in the outer and inner surface of the probe monitor metal temperatures. From these values the heat flux is calculated.

[0064] In addition to the baseline heat-flux probe, an HVT was used to measure the true gas temperature at the same location. The probe is water-cooled to protect its stainless steel outer shell from the intense heat of the combustion flame. A Type S thermocouple runs down its center and is shielded from the radiation of the flame and refractory walls by a tip made from insulation board. A vacuum pump is used to draw gases past the thermocouple junction at a rate sufficient to achieve a velocity past the thermocouple junction of 120 m/sec. At this velocity, the radiative component to heat transfer is minimized and convective heat transfer is dominant. In this manner, the true gas temperature can be obtained without the interference of radiation to or from the thermocouple junction.

[0065] Fly ash samples were obtained by various means at the inlet and outlet of the pilot plant ESP or BH. U.S. Environmental Protection Agency (EPA) Method 5 was used to establish particulate matter (PM) concentrations in the flue gas. High- volume sample extraction and the pilot plant control device collection hoppers can provide large samples for study.

[0066] Residual fuel oil samples were heated to lower the fuel viscosity prior to atomization in the burner. Fuel additives were added to the heated fuel stream near the atomizing nozzle by means of a specially designed metered injection system. In the injection system a fuel flow meter was used to ascertain fuel flow, the output was fed to a PID controller which then controlled the flow rate of a chemical metering pump. The concentration of the fuel additive was dynamically adjusted to any change in flow rate of the fuel. The output of the metering pump was injected into the flowing heated fuel producing a dispersion of droplets of the fuel additive in the fuel. This mixture then traversed a static mixing section which insured that the treated fuel was homogeneously mixed with the fuel before entering the atomizing section of the burner.

[0067] Tests were conducted for three days at the EERC facility with a furnace exit gas temperature (FEGT) between 1250°C and 1315°C and at an excess air level at or near 10%. This corresponds to approximately 2.0% oxygen in the flue gas at the furnace exit. The residual fuel oil firing rate and the combustion air flow rates were adjusted during each of these tests to maintain these levels. On the fourth day, each test performed at an FEGT between 1250°C and 1315°C and at an excess air level at or near 5%. Tables 2 through 7 provide baseline and run-average summaries of operating conditions for each test period during each day of testing. Control of the residual fuel oil feed rate was accomplished by adjusting the set point on the speed controller of the pump. The controller then adjusted pump speed to maintain the feed rate at the desired level. Excess air levels were achieved by manually adjusting valve positions on each of the primary and secondary air streams. A BH was used for particulate control during all test periods.

[0068] The furnace was preheated to 1290°C with natural gas for up to 8 hours prior to the start of each day's testing. Furnace pressure was maintained near –1 torr by adjustment of a control valve blending ambient air into the duct at the inlet of the induced-draft fan.

[0069] Two banks of analyzers monitored gaseous emissions and were designated as furnace exit and BH exit in each of the following Tables 2 through 6. Furnace exit analyses were sampled approximately 1 meter downstream of the fouling probe bank. This oxygen level was used to control excess air levels during each test. BH exit analyses are normally obtained from the ductwork following BH. Because of the higher vacuum at the back end of the test system and the large number of flanged connections, air leakage into the ductwork resulted in a 1-2% increase in flue gas oxygen concentrations. The oxygen analysis from each bank of analyzers was used to correct gaseous emissions of interest to a constant excess air level of 20% (3.5% O_2). The calculation used to correct emissions levels reported here is:

$$\text{Corrected } SO_2\text{, ppm} = \frac{[\text{Actual } SO_2\text{, ppm}] \times [21 - 3.5 \text{ (Target } O_2\text{, \%)}]}{[21 - \text{Actual } O_2\text{, \%}]}$$

[0070] Gas analyzers were routinely zeroed and spanned prior to the start of each test. Additional calibration of the analyzers was performed when results were suspect or unexpected.

[0071] In Tests AF-CTS-751, 753, 755, 756-1, and 758 (twice), the primary objective was to establish baseline operating characteristics, emissions rates for the various gas species, and the work produced under the various operating conditions. In addition, fly ash samples were collected to determine the dust loading (or PM) of the gas stream entering the BH. Results from these tests are provided in Table 2 through 6. Once stable combustion conditions had been achieved after switching from natural gas to residual fuel oil, a series of measurements were made using an HVT, a baseline heat-flux probe, and a small cyclone to obtain fly ash samples. The swirl setting on the secondary air stream was held constant at 3.5 for all test periods performed during this test series.

[0072] In all other tests, the primary objective was to establish the effectiveness of various fuel additives for lowering regulated gaseous emissions and increasing the work produced. The same test protocol was used here to determine the effectiveness of the fuel additives. Results from these tests are provided in Tables 2 through 7. As part of the test protocol, a period of baseline operation typically preceded all test periods where a fuel additive was evaluated.

[0073] Following are the fuel additive formulations used in this study:

[0074] Additive 2: 5 mL meadowfoam oil (d = 0.91 g/mL); 5.1 g fescue extract (hexane extracted); and 995 mL AROMATICS 150 FLUID (d = 0.90 g/mL); not prepared in a glove box;

[0075] Additive 5: 5 mL meadowfoam oil (d = 0.91 g/mL); 5.2 g alfeque extract (hexane extracted); 2 mL 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline (d = 1.03); 1.6 g ISOMIXTENE®; and 993 mL AROMATIC 100 FLUID (d = 0.87 g/mL); prepared in a glove box under non-oxygenation conditions;

[0076] Additive 6: 80% (v/v) Component 1 and 20% (v/v) Component 2 where: Component 1: 5 mL meadowfoam oil (d = 0.91 g/mL); 5.1 g alfeque extract (hexane extracted); and 995 mL AROMATICS 150 FLUID (d = 0.90 g/mL); not prepared in a glove box; Component 2: 2-ethylhexyl nitrate.

[0077] Additive 7: 80% (v/v) Additive 5 and 20 % (v/v) 2-ethylhexyl nitrate.

[0078] Additive 8: 0.5 mL 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline (d = 1.03); 0.8 g ISOMIXTENE®; 2.5 mL meadowfoam oil (d = 0.91); 0.39 g fescue extract (hexane extracted); and 500 mL AROMATIC 100 FLUID (d = 0.87); prepared in a glove box under non-oxygenation conditions.

[0079] Additive 9: 0.5 mL 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline (d = 1.03); 0.8 g ISOMIXTENE®; 2.5 mL meadowfoam oil (d = 0.91); 0.39 g alfeque extract (ethanol extracted); and 500 mL AROMATIC 100 FLUID (d = 0.87); prepared in a glove box under non-oxygenation conditions.

[0080] Additive 10: 0.5 mL 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline (d = 1.03); 0.8 g ISOMIXTENE®; 2.5 mL meadowfoam oil (d = 0.91); 0.39 g alfeque extract (hexane extracted); and 500 mL AROMATIC 100 FLUID (d = 0.87); prepared in a glove box under non-oxygenation conditions.

[0081] The following tables provide testing results for residual fuel oils and the listed fuel additives.

Table 2. Baseline and Test Run-Average Operating Parameters – AF-CTS-745

Test Number **Description**	**AF-CTS-745** **Residual Fuel Oil**	**AF-CTS-745** **Residual Fuel Oil**	**AF-CTS-745** **Residual Fuel Oil**

Day	**1**		**1**		**1**	
Test Period	1		2		3	
Time	11:13–12:13		16:26–17:26		17:36–17:58	
Swirl Setting	3.5		3.5		3.5	
Fuel Feed Rate, kg/hr	16.6		15.9		15.6	
Firing Rate, MJ/hr	728.77		705.00		691.54	
Additive	None		Additive 2		Additive 2	
Addition Rate, mL/hr	N/A		30		60	
Flue Gas Analysis	Furnace Exit	BH Exit	Furnace Exit	BH Exit	Furnace Exit	BH Exit
O_2, %	2.19	3.22	2.06	3.02	1.92	2.77
CO_2, %	14.23	13.14	14.13	12.88	14.19	12.79
SO_2, ppm	1716	1687	1717	1681	1707	1678
NO_x, ppm	169	131	161	106	156	128
CO, ppm	4.20	12.03	4.58	11.98	4.56	12.18
Excess Air, %	11.11		10.38		9.61	
Emissions at 3.5% O_2						
SO_2, ppm	1733	1803	1722	1776	1700	1749
SO_2, g/MJ	5.90	6.13	5.86	6.05	5.80	5.97
NO_x, ppm	171	140	162	112	155	133
System Temperatures, °C						
Forced Draft Fan Outlet	63.3		66.1		66.1	
Primary Air	283		281		279	
Secondary Air	341		341		340	
FEGT	1286		1288		1282	
BH Inlet	179		176		176	
BH Outlet	146		144		144	
Stack	82.8		95		93.3	
Oil Feed	88.9		88.9		89.4	
Heat Flux Probe						
Temperatures, °C						
HVT	1334		1353		1343	
Surface Metal 1	982.7		957.8		948.9	
Surface Metal 2	963.3		938.9		920.6	
Back Metal 1	740.5		701.7		693.9	
Back Metal 2	687.8		662.2		652.8	
Water Out	25.9		29.4		29.9	

Water In	18.7	20.7	20.6
Water Flow, l/min	3.37	2.99	2.97
Heat Flux, MJ/m^2-hr	1011	1073	1154
Burner Quarl Deposit Found	Yes	Yes	No

Table 3. Baseline and Test Run-Average Operating Parameters – AF-CTS-753

Test Number	**AF-CTS-753**		**AF-CTS-753**		**AF-CTS-753**	
Description	**Residual Fuel Oil**		**Residual Fuel Oil**		**Residual Fuel Oil**	
Day	**2**		**2**		**2**	
Test Period	4		5		6	
Time	8:38-11.01		11:33-12:57		14:20-14:35	
Swirl Setting	3.5		3.5		3.5	
Fuel Feed Rate, kg/hr	17.5		17.0		15.4	
Firing Rate, MJ/hr	775.70		752.45		681.34	
Additive	None		Additive 5		Additive 5	
Addition Rate mL/hr	N/A		30		60	
Flue Gas Analysis	Furnace Exit	BH Exit	Furnace Exit	BH Exit	Furnace Exit	BH Exit
O_2, %	2.02	2.68	2.03	2.85	2.12	2.91
CO_2, %	14.47	13.37	14.33	13.57	14.24	13.49
SO_2, ppm	1688	1681	1737	1712	1714	1691
NO_x, ppm	207	173	203	174	205	176
CO, ppm	4.57	16.11	3.98	15.25	3.84	15.53
Excess Air, %	10.61		10.22		10.72	
Emissions at 3.5% O_2						
SO_2, ppm	1702	1743	1740	1792	1725	1776
SO_2, g/MJ	6.05	6.53	6.30	6.55	6.26	6.51
NO_x, ppm	207	179	203	182	206	185
System Temperatures, °C						
Forced Draft Fan Outlet	58.9		60.6		62.8	
Primary Air	300		300		301	
Secondary Air	341		341		341	
FEGT	1275		1285		1292	
BH Inlet	175		175		176	
BH Outlet	143		143		143	
Stack	83.9		88.3		90.6	

Oil Feed	93.3	95	93.3
Heat Flux,			
Temperatures, °C			
HVT	1354	1366	N/A
Surface Metal 1	981.7	955	N/A
Surface Metal 2	978.9	947.8	N/A
Back Metal 1	702.2	676.1	N/A
Back Metal 2	688.9	640.6	N/A
Water Out	29.6	30.1	N/A
Water In	20.6	20.7	N/A
Water Flow, l/min	3.01	2.91	N/A
Heat Flux, MJ/m^2-hr	1126	1129	N/A
Method 5 Sample Taken	No	Yes	No

Table 4. Baseline and Test Run-Average Operating Parameters – AF-CTS-753 (cont.) & 754

Test Number	**AF-CTS-753**		**AF-CTS-754**	
Description	**Oil**		**Oil**	
Day	**2**		**2**	
Test Period	7		8	
Time	14:35-15:06		15:37–16:53	
Swirl Setting	43.5		3.5	
Fuel Feed Rate, kg/hr	17.1		16.2	
Firing Rate, MJ/hr	758.50		719.34	
Additive	Additive 5		Additive 6	
Addition Rate, mL/hr	15		40	
Flue Gas Analysis	Furnace Exit	Baghouse Exit	Furnace Exit	Baghouse Exit
O_2, %	1.80	2.59	2.00	2.79
CO_2, %	14.49	13.74	14.38	13.55
SO_2, ppm	1750	1721	1717	1696
NO_x, ppm	199	171	211	182
CO, ppm	4.18	15.90	4.20	15.80
Excess Air, %	8.96		10.0	
Emissions at 2.0% O_2				
SO_2, ppm	1732	1776	1717	1770
SO_2 g/MJ	6.28	6.51	6.19	6.49

NO_x, ppm	197	176	190	211
System Temperatures, °C				
Forced Draft Fan Outlet	62.8		62.8	
Primary Air	300		282	
Secondary Air	341		340	
FEGT	1293		1284	
Baghouse Inlet	176		173	
Baghouse Outlet	143		142	
Stack	91.1		88.3	
Oil Feed	91.7		91.7	
Heat Flux Probe				
Temperatures, °C				
HVT	N/A		1343	
Surface Metal 1	N/A		972.2	
Surface Metal 2	N/A		946.7	
Back Metal 1	N/A		683.3	
Back Metal 2	N/A		643.9	
Water Out	N/A		30.5	
Water In,	N/A		21.3	
Water Flow, l/min	N/A		2.85	
Heat Flux, MJ/m^2-hr	N/A		1086	
Method 5 Sample Taken	No		No	

Table 5. Baseline and Test Run-Average Operating Parameters – AF-CTS-755

Test Number	**AF-CTS-755**		**AF-CTS-755**		**AF-CTS-745**	
Description	**Oil**		**Oil**		**Oil**	
Day	**3**		**3**		**3**	
Test Period	9		10		11	
Time	9:20-9:44		9:48-10:14		10:15-10:41	
Swirl Setting	3.5		3.5		3.5	
Fuel Feed Rate, kg/hr	17.2		16.5		16.9	
Firing Rate, MJ/hr	761.88		730.94		746.65	
Additive	None		Additive 7		Additive 7	
Addition Rate, mL/hr	N/A		40		80	
Flue Gas Analysis	Furnace Exit	BH Exit	Furnace Exit	BH Exit	Furnace Exit	BH Exit
O_2, %	1.80	2.78	1.95	2.94	1.90	2.92

CO_2, %	14.55	14.01	14.42	13.87	14.46	13.88
SO_2, ppm	1773	1707	1751	1696	1753	1693
NO_x, ppm	182	167	185	170	185	168
CO, ppm	6.82	19.22	7.05	18.18	10.46	22.44
Excess Air, %	8.96		9.77		9.50	
Emissions at 2.0% O_2						
SO_2, ppm	1755	1780	1746	1784	1744	1779
SO_2, g/MJ	6.32	6.32	6.32	6.34	6.32	6.34
NO_x, ppm	180	174	185	179	184	177
System Temperatures, °C						
Forced Draft Fan Outlet	61.1		61.7		62.2	
Primary Air	284		283		283	
Secondary Air	342		342		342	
FEGT	1274		1273		1276	
BH Inlet	178		177		177	
BH Outlet	145		144		144	
Stack	90		90.6		90.6	
Oil Feed	93.9		93.3		93.3	
Heat-flux Probe						
Temperatures, °C						
HVT	1288		1299		N/A	
Surface Metal 1	935		939.4		N/A	
Surface Metal 2	912		917.8		N/A	
Back Metal 1	655		662.8		N/A	
Back Metal 2	622.8		633.3		N/A	
Water Out	30.07		30.38		N/A	
Water In	21.41		21.59		N/A	
Water Flow, l/min	2.79		2.75		N/A	
Heat Flux, MJ/m^2-hr	997.6		998.5		N/A	
Method 5 Sample Taken	No		No		No	

Table 6. Baseline and Test Run-Average Operating Parameters – AF-CTS-756 & 757

Test Number	**AF-CTS-756-1**	**AF-CTS-756-2**	**AF-CTS-747**
Description	**Oil**	**Oil**	**Oil**
Day	**4**	**4**	**4**
Test Period	12	13	14
Time	9:19-11:00	11:02-12:26	13:19-15:14

Swirl Setting	3.5		3.5		3.5	
Fuel Feed Rate, kg/hr	16.3		16.0		15.8	
Firing Rate, MJ/hr	723.13		707.01		701.21	
Additive	None		Additive 8		Additive 9	
Addition Rate, mL/hr	N/A		40		40	
Flue Gas Analysis	Furnace Exit	BH Exit	Furnace Exit	BH Exit	Furnace Exit	BH Exit
O_2, %	0.98	1.71	1.03	1.77	1.14	1.87
CO_2, %	15.22	14.48	15.19	14.42	15.07	14.35
SO_2, ppm	1796	1861	1867	1847	1845	1856
NO_x, ppm	186	175	193	180	176	172
CO, ppm	43.0	65.0	12.5	22.4	10.3	18.8
Excess Air, %	4.68		4.94		5.49	
Emissions at 2.0% O_2						
SO_2, ppm	1794	1833	1776	1825	1765	1843
SO_2. g/MJ	6.14	6.68	6.38	6.66	6.36	6.72
NO_x, ppm	177	172	184	178	168	171
System Temperatures, °C						
Forced Draft Fan Outlet	55		56.1		57.8	
Primary Air	270		269		269	
Secondary Air	338		338		338	
FEGT	1287		1289		1286	
BH Inlet	171		179		178	
BH Outlet	138		144		144	
Stack	72.8		77.2		81.1	
Oil Feed	90.6		88.3		89.4	
Heat-flux Probe						
Temperatures, °C						
HVT	1288		1290		1296	
Surface Metal 1	961.7		967.8		955	
Surface Metal 2	948.3		945		932	
Back Metal 1	696.1		702.8		700.6	
Back Metal 2	666.1		672.2		671.1	
Water Out	29.42		29.93		30.44	
Water In	20.19		20.79		22.11	
Water Flow, l/min	2.66		2.61		2.46	
Heat Flux, MJ/m^2-hr	1020		983.4		848.4	

Method 5 Sample Taken	Yes	Yes	Yes

Table 7. Baseline and Test Run-Average Operating Parameters – AF-CTS-758

Test Number	AF-CTS-758		AF-CTS-758		AF-CTS-748	
Description	Oil		Oil		Oil	
Day	4		4		4	
Test Period	15		16		17	
Time	15:27-15:48		15:48-17:06		17:06-17:34	
Swirl Setting	3.5		3.5		3.5	
Fuel Feed Rate, kg/hr	15.9		15.9		15.8	
Firing Rate, MJ/hr	705.56		706.53		702.66	
Additive	None		Additive 10		None	
Addition Rate, mL/hr	N/A		40		N/A	
Flue Gas Analysis	Furnace Exit	BH Exit	Furnace Exit	BH Exit	Furnace Exit	BH Exit
O_2, %	1.14	1.87	1.09	1.84	1.14	1.86
CO_2, %	15.09	14.45	15.11	14.38	15.07	14.35
SO_2, ppm	1844	1845	1844	1850	1837	1836
NO_x, ppm	177	168	180	172	183	174
CO, ppm	11.7	21.6	11.8	22.0	8.6	18.3
Excess Air, %	5.49		5.24		5.49	
Emissions at 2.0% O_2						
SO_2, ppm	1764	1832	1760	1835	1757	1823
SO_2, g/MJ	6.34	6.64	6.34	6.68	6.32	6.64
NO_x, ppm	169	167	172	171	175	173
System Temperatures, °C						
Forced Draft Fan Outlet	58.3		58.9		58.9	
Primary Air	269		269		269	
Secondary Air	338		338		338	
FEGT	1289		1291		1290	
BH Inlet	178		176		177	
BH Outlet	145		144		144	
Stack	85		85		85.6	
Oil Feed	89.5		89.4		90	
Heat-Flux Probe						
Temperatures, °C						

HVT	N/A	1296	N/A
Surface Metal 1	850	906.7	917.2
Surface Metal 2	840	868.3	875.6
Back Metal 1	571.7	606.1	632.8
Back Metal 2	551.1	585	592.2
Water Out	30.69	30.34	30.46
Water In	22.07	22.34	22.47
Water Flow, l/min	2.95	2.94	2.91
Heat Flux, MJ/m^2-hr	1052	966.9	957.9
Method 5 Sample Taken	No	Yes	No

[0082] Initial shakedown testing began the day before actual testing and included firing the baseline residual fuel oil to establish the effectiveness of changes that had been made to the system following the first series of fuel additive tests performed earlier. This shakedown period verified that the changes made improved the overall operability of the system. Included among the many changes made were the addition of insulation to various system feed lines, the piping of steam to the burner gun for use as the atomizing fluid for the oil, the addition of a mixing section in the fuel feed line, and the addition of steam heaters on the storage barrel that was used to fill the feed tank so as to maintain a residual fuel oil temperature at or near 240°F. The result of the changes allowed the fuel to be fed continuously through the burner gun with no carbon deposits forming on the gun or the air piping within the burner quarl.

[0083] The FEGT was maintained near 2350°F for all test periods. In some cases, it was allowed to rise to see the effect of the fuel additive on the work produced, and in other cases, it was maintained during fuel additive injection to determine the level of fuel savings achieved while maintaining the same level of work produced. Because the changes in fuel and operating parameters provided a very stable combustion environment, the combustion efficiency was very high for all test periods. This made it difficult to monitor changes in the combustion environment resulting from fuel additive addition. Changes in the combustion environment were noted, though, during this period and are detailed below. Because of the difficulty of monitoring changes, the excess air level was lowered to approximately 5% during the final day of testing on Day 4.

[0084] Two banks of analyzers, one at the furnace exit and one at the BH outlet, were used to determine the concentration of the combustion products in the gas stream. Measurements of flue gas O_2, CO, CO_2, SO_2, and NO_x were continuously monitored and recorded by the CTF data acquisition system. Test period averages have been provided in Tables 2 through 7.

[0085] Excess air levels fluctuated with changes in the fuel feed rate and varied from around 9% to 11% during the tests conducted from June 21 through June 23. Corrected SO_2 emissions were fairly steady at an average of approximately 1720 ppm ± 20 ppm for all test periods near 10% excess air.

[0086] An analysis of the data indicates that each of the analytical observables is a strong function of the excess air. When a spline fit is drawn through the data points, one gets a much better comparison view than if the data is globally fit. Furnace and baghouse data are treated separately. Looking at the NO_x and CO data for both the furnace and the baghouse (Figures 7 and 8, respectively), one finds that the results for one of the treated runs are consistently lower than those of the baseline measurements at equal excess air. Additive 2 shows a consistent improvement in gaseous emissions. Surprisingly, this fuel additive shows its effect even though it was only used in experiments with excess air of about 10%.

[0087] Particulate Matter (PM) emission values measured and expressed as dust loadings were obtained at the BH inlet during a number of test periods using U.S. Environmental Protection Agency Method 5 PM sampling. Such testing provided significant evidence of the effectiveness of various fuel additives in improving the combustion characteristics of the residual fuel oil (see Figure 9). During the baseline test on Day 4 (Test Period 12), the dust loading entering the BH was determined to be 0.122 g/m^3. During Test Period 5, Additive 5 was injected at a rate of 30 mL/hr where EPA Method 5 dust loading was significantly reduced to 0.0677 g/m^3, a 44.6% reduction. In Test Period 13, Additive 8 was utilized at an addition rate of 40 mL/hr as was Additive 10 in Test Period 16. EPA Method 5 dust loading was reduced during the use of Additive 8 to 0.0886 g/m^3 and to 0.0959 g/m^3 during the use of Additive 10. This translates to a 27.5% reduction and a 21.5% reduction, respectively. It should be noted that the excess air levels during Test Period 5 (Additive 5) were higher than they were for Test Period 12, the baseline test period, so a portion of the reduction noted here can be accounted for by the increase in available oxygen. However, this was not the case for Test Periods 13 (Additive 8) and 16 (Additive 10). Excess air levels were approximately the same during the baseline test period as they were for the two noted testing periods.

[0088] While heat flux behavior is a complicated function, it is assumed to be a function of at least the fuel firing rate and the excess air. Figure 10 plots the heat flux as measured at EERC divided by the fuel firing rate versus excess air reported. The data demonstrates that the heat flux/fuel ratio produced for fuel treated with Additive 2 was greater than that seen for the untreated fuel. An improvement of from 7.6% to 10.1% in heat flux ratio was seen for Additive 2.

[0089] An infrared (IR) camera/recorder was used to evaluate any changes in flame temperature that might occur between periods of baseline operation and fuel additive injection. Results from these measurements have been summarized in Table 8. It would appear from the data below that the most telling trend in flame temperature was the oil feed rate. This relationship can be seen in Figure 6. The equation of the linear regression line has been provided and the R^2 value calculated. The flame temperature does not fit a linear relationship with feed rate well, but does trend in that direction. Although the test furnace was operated at a similar furnace exit gas temperature during each day of operation, the corresponding flame temperature varies significantly from day to day, as does the feed rate required to achieve that temperature. This indicates that the heat flux through the furnace walls tends to change from day to day. However, within a single day's operation only small trends may be noted.

[0090] During the first day of testing, the recorded flame temperature just prior to fuel additive injection and immediately following injection of Additive 2 remained constant at 1333 °C. The feed rate was also constant. However, during the second day of testing, the baseline feed rate (Test Period 4) was considerably higher than during fuel additive injection. Flame temperature readings from the IR camera were constant at 1402 °C during Test Periods 5 and 7 with the injection of Additive 5 at the 30 mL/hr and 15 mL/hr rate, respectively. This would indicate some effect of the fuel additive on heat release in the furnace. During Test Period 8, Additive 6 was injected at the 40 mL/hr rate. While the flame temperature decreased to 1392 °C, the feed rate was significantly reduced from baseline levels during this period to 16.23 kg/hr.

Table 8. Summary of IR Camera Recorder Data

Test Period	Day	Additive	Injection Rate, (mL/hr)	Oil Feed Rate, (kg/hr)	IR Flame Temp. (°C)
1	Day 1	None	None	15.02	1333
2	Day 1	Additive 2	30	15.91	1333
4	Day 2	None	None	17.50	1402
5	Day 2	Additive 5	30	16.98	1402
7	Day 2	Additive 5	15	17.12	1402
8	Day 2	Additive 6	40	16.23	1392
9	Day 3	None	None	17.19	1366
10	Day 3	Additive 7	40	16.50	1366
12	Day 4	None	None	16.32	1371
13	Day 4	Additive 8	40	15.95	1359
14	Day 4	Additive 9	40	15.82	1359
15	Day 4	None	None	15.92	1362
16	Day 4	Additive 10	40	15.94	1360

[0091] The baseline flame temperature of 1366 °C was achieved in Test Period 9 with a feed rate of 17.19 kg/hr of residual fuel oil. After the injection of Additive 7 at the 40 mL/hr rate, the flame temperature remained constant at a lower feed rate of 16.50 kg/hr. This represents a reduction in feed of approximately 4%. During the final day of testing, the initial baseline flame temperature was recorded at 1371°C (Test Period 12). Although the temperature dropped to 1359 °C during the injection of Additives 8 and 9, it remained relatively constant throughout the day, rising to 1362°C during the baseline Test Period 15 that followed. Essentially no change occurred during Test Period 16 when injecting Additive 10 at the 40 mL/hr rate. The flame temperature held constant at 1360 °C.

CANMET Research Furnace Testing

[0092] Testing was also conducted at the CANMET Research Furnace in Ottawa, Canada. The residual fuel oil used in the tests was obtained from PROVMAR Fuels Inc. of Hamilton, Ontario. The properties for the residual fuel oil are listed in Table 9. Such residual fuel oil has a moderate sulfur content of about 1.7%, with a very high heating value of 42.12 MJ/kg at a moisture content of 0.05%. The proximate, ultimate, and heating value analyses for the residual fuel oil tested are also provided in Table 1 along with the theoretical emission limit of sulfur.

Table 9

Grade ISO 8217:05 RMG380			
Property	Result	Specification	Test Method
Density, kg/m3 @ 15°C	1021.3	991.0 Max	ISO 12185
Viscosity cst @ 50°C	513.5	380.0 Max	ISO 3104
Viscosity cst @ 80°C	94.4	Max	ISO 3104
Flash Point, °C	110°	60.0° Min	ISO 2719
Pour Point, °C	0°	30° Max	ISO 3016
MCR, % m/m	13.92	18.00 Max	ISO 10370
Ash, % m/m	0.066	0.150 Max	ISO 6245
Water, % v/v	0.05	0.50 Max	ISO 3733
Sulfur, %m/m	1.73	4.50 Max	ISO 8754
Compatibility, Spot#	1	2 Max	ASTM 474
Vanadium, mg/kg	107	300 Max	ASTM D5863
Sodium, mg/kg	14	Max	ASTM D5863
Silicon, mg/kg	34	Max	ISO 10478
Aluminum, mg/kg	39	Max	ISO 10478
Al & Si, mg/kg	73	80 Max	CALC.
Fe, mg/kg:	13.4	Max	ASTM D5863

Pb, mg/kg:	0	Max	ASTM D5863
Zn, mg/kg:	0	Max	ASTM D5863
Mg, mg/kg:	0	Max	ASTM D5863
Ca, mg/kg:	2	Max	ASTM D5863
Ni, mg/kg:	25.6	Max	ASTM D5863
K, mg/kg:	2.3	Max	ASTM D5863
Total Sed, Pot., % m/m	0.04	0.10 Max	ISO 10307-2
Asphaltenes, % m/m:	7.1		ASTM D3279
CCAI, Index#	879	860	

Net Cal, Val, MJ/Kg (ASTM D4868)	42.12
Gross Heating Value (ASTM D4868)	
BTU/lb	18109
BTU/Gal	154122
Injection Temp 10cst, °C	151
Injection Temp 15cst, °C	134
Min Pump Temp 1,000cst, °C	41
Ultimate Analysis (ASTM5291)	
C, % weight	87.79
H, % weight	10.4
N, % weight	0.38

[0093] The residual fuel oil was stored cold prior to testing. A day tank was used to heat the residual fuel oil to 121°C and to keep the fuel hot during testing.

[0094] In this test protocol the furnace control was primarily based on the fuel flow into the furnace. The fuel flow was held constant along with the air flow. A calorimetric section of the furnace allowed one to determine the heat transfer from the furnace as a function of distance from the burner. There was no "baghouse" in this system and the furnace exit temperature was allowed to float.

[0095] When firing a liquid fuel such as residual fuel oil, a pump is used to convey the fuel through a dual-fluid atomizer into the combustion chamber. In this furnace, compressed air is used as the atomizing fluid. Combustion air is preheated by an electric air heater.

[0096] Flame stability is assessed by observation of the flame via a quartz observation port located along the longitudinal axis of the furnace at the furnace end opposite the burner. Under normal operation a video camera was used to qualitatively assess the flame quality and to create a video record of the flame characteristics occurring during an experiment.

[0097] The general test method sets the burner at its maximum level of swirl and monitors system parameters such as fuel feed rate, excess air, gaseous emissions (O_2, CO_2, CO, SO_2, and NO_x), combustor static, and air flow rates. Photographs of the flame and burner zone are then taken through a sight port in the furnace just above the burner cone using a video camera.

[0098] The CANMET furnace uses two banks of gas analyzers to monitor O_2, CO, CO_2, and NO_x. Sulfur dioxide (SO_2) is also monitored. The analyzers are typically located at the furnace exit and the particulate control device exit. The gas analyses are reported on a dry basis. The flue gas constituents are monitored and recorded by the data acquisition system at 10 second intervals during the experiment. Statistical characteristics of the measured quantities were used to establish confidence limits on the measured data.

[0099] In the calorimetric section of the furnace, inlet and exit temperatures are monitored at 10 second intervals and recorded by the data acquisition system. The flow rates of the therminol working fluid are also measured and accessible via the data acquisition system. From these measurements the heat transfer in the furnace can be determined as a function of time for each of the 28 calorimetric bands along the long axis of the furnace.

[00100] Ash samples were obtained by various means at the inlet and outlet of the pilot plant ESP or BH. Isokinetic gas sampling is used to establish particulate matter (PM) concentrations in the flue gas. High volume sample extraction and the pilot plant control device collection hoppers can provide large samples for study. Chemical composition was also determined for the collected ash samples. Collection of the isokinetic dust samples required approximately 3 hrs per sample. There was only one ash sample collected per run.

[00101] The residual fuel oil was heated to lower its viscosity prior to atomization in the burner. Fuel additives were added to the heated fuel stream near the atomizing nozzle by means of a specially designed metered injection system. In the injection system a fuel flow meter was used to ascertain fuel flow, the output was fed to a PID controller which controlled the flow rate of a chemical metering pump. The concentration of the fuel additive was dynamically adjusted to any change in flow rate of the fuel. The output of the metering pump was injected into the flowing hot fuel producing a dispersion of droplets of the fuel additive in the warm fuel. This mixture then traversed a static mixing section to homogeneously mix the fuel additive with the fuel before entering the atomizing section of the burner.

[00102] Tests performed at the CANMET research furnace were performed with furnace operation specified by fuel flow rate and excess air level, both of which were controlled by the furnace operator. The furnace was preheated with natural gas for up to 5 hrs prior to beginning experiments on residual fuel oil. Standard start up protocol involved collection of data with untreated fuel oil burning in the system for at least one hour prior to beginning any experimental treatment. This protocol enabled one to verify baseline behavior on each day of

operation. The experiments were designed to investigate the effects of the chemical additives on furnace operation at two different excess air concentrations (10% and 7.5%). Baseline operation of the fuels was determined at the beginning and end of test campaigns as well as at the start of each test day.

[00103] In the testing, all of the fuel additives were evaluated at the 10% excess air level, and only the best performers were evaluated at the lowered excess air level. The fuel additive compositions for the CANMET testing were prepared as follows with additives containing ISOMIXTENE® (Additives 13 and 14) prepared under inert atmosphere in a glove box, and additives without ISOMIXTENE® (Additives 11, 12, 15, and 16) prepared under normal atmospheric conditions.:

[00104] Additive 11 was prepared by mixing 13.9 grams of fescue extract and 10 mL of meadowfoam oil, and then blending the mixture with AROMATIC 150 FLUID up to 2000 mL.

[00105] Additive 12 was prepared by mixing 13 grams of fescue extract, 10 mL of meadowfoam oil and 1 mL of SANTOQUIN®, and blending the mixture with AROMATIC 150 FLUID up to 2000 mL.

[00106] Additive 13 was prepared by mixing 5.12 grams of fescue extract, 5 mL of meadowfoam oil, 10 drops of SANTOQUIN®, and 0889 grams of ISOMIXTENE®, and blending the mixture with AROMATIC 150 FLUID up to 1000 mL.

[00107] Additive 14 was prepared by mixing 5.13 grams of alfalfa extract, 5 mL of meadowfoam oil, 10 drops of SANTOQUIN®, and 088 grams of ISOMIXTENE®, and blending the mixture with AROMATIC 150 FLUID up to 1000 mL.

[00108] Additive 15 was prepared by mixing 13 grams of alfalfa extract, 10 mL of meadowfoam oil, and 2 mL of SANTOQUIN®, and blending the mixture with AROMATIC 150 FLUID up to 2000 mL.

[00109] Additive 16 was prepared by mixing 13 grams of alfalfa extract, and 10 mL of meadowfoam oil, and blending the mixture with AROMATIC 150 FLUID up to 2000 mL.

[00110] Table 10 summarizes the observations for particulate matter concentration in the CANMET tests performed at 10% excess air. The carbon content of the ash collected from the treated fuel experiments were uniformly lower than that seen in the reference system, but the overall isokinetic dust loading showed modest increases for Additives 11 and 12. At a lower excess air ratio the carbon content of the collected ash was consistent with the isokinetic dust loading as shown in Table 11. Additive 15 showed consistent reduction in particulate loading.

Table 10. CANMET Testing: Particulate Matter Concentration at 10% Excess Air level

Test Run	Isokinetic Dust Loading (mg/m^3)	Ash Carbon Content (% Carbon)	Carbon Reduction (%)
Reference	129	79.9%	-
Additive 11	150	77.5%	-13%
Additive 12	144	78%	-9%
Additive 13	119	71.1%	18%
Additive 14	119	72.7%	16%
Additive 15	105	74.7%	24%
Additive 16	124	75.7%	9%

Table 11. Dust Loading Results 7.5% Excess Air.

Test Run	Isokinetic Dust.Loading (mg/m^3)	Ash Carbon Content (% Carbon)	Carbon Reduction (%)
Reference	208	75.4	-
Additive 12	134	66.9	42.8
Additive 14	232	79.2	-17.0
Additive 15	160	67.6	31.0
Additive 16	200	78.4	0

[00111] Qualitatively, the flames for several of the treated fuels appeared shorter and brighter than the flames observed for the reference (untreated) fuels. This observation is supported by the flame video, but is difficult to quantify. A shorter more dense flame should provide maximum heat transfer in the calorimetric section of the furnace. Data supporting this is found in Tables 12 and 13 for experiments performed at both 10% and 7.5% excess air. Data was collected every 10 seconds to build a large statistical sample. The standard deviation of this data set provides an estimate of uncertainty. The measured therminol heat uncertainty is about 1%. The measured flue gas heat uncertainty is about 0.1%. Heat Disposition changes above 2% are statistically significant at the 95% confidence level

Table 12. Heat Disposition from Available Heat at 10% Excess Air

Test Run	Heat to Therminol	Heat to Flue Gas	"Lost Heat"	Lost Heat Reduction
Reference	62.7%	8.8%	28.5%	-
Additive 11	65.9%	9.2%	24.9%	3.6%
Additive 12	65.9%	9.0%	25.1%	3.4%
Additive 13	64.9%	8.8%	26.3%	2.2%

Additive 14	67.3%	8.9%	23.8%	4.7%
Additive 15	64.1%	9.1%	26.8%	1.7%
Additive 16	66.2%	9.2%	24.6%	3.9%

Table 13. Heat Disposition from available Energy at 7.5% Excess Air

Test Run	Heat to Therminol	Heat to Flue Gas	"Lost Heat"	Lost Heat Reduction
Reference	62.7%	9.16%	28.1%	-
Additive 12	64.1%	9.67%	26.2%	1.9%
Additive 14	65.6%	9.45%	24.9%	3.2%
Additive 15	63.8%	9.37%	26.8%	1.3%
Additive 16	65.4%	9.41%	25.2%	2.9%

IPT Laboratory Testing

[00112] Testing was also run at the IPT Laboratory Test Facility in Sao Paulo, Brazil. The IPT test furnace is operated similarly to that at CANMET. The IPT test facility employs a horizontal burner, Model MPR, manufactured by ATA Combustao Tecnica of Brazil that is fitted with an external water-cooled jacket. The fuel charge rate and excess air of the flue gas are taken as independent variables and the other observables are treated as dependent variables. The furnace contains a calorimetric section. One significant difference in the experiments performed in Brazil is related to the fuel. Brazilian fuel specifications are significantly different than those adopted in the United States. For example, the density and asphaltene content of the residual fuels commonly used in Brazil are significantly greater than those commonly used in the United States. At these very high asphaltene and viscosity levels, pollution caused by unburned carbon (particulate matter) is of primary importance. Part of the strategy to minimize this problem involves combusting the fuel under very high excess oxygen conditions. Standard operating procedure in Brazil calls for operating a furnace at furnace exit oxygen content of about 7% or about 37.5% excess air.

[00113] The fuel additive evaluated at IPT contained a combination of plant extract and an organometallic iron complex. In particular, 49.2 grams of alfalfa extract were mixed with 7.57 mL of SANTOQUIN® antioxidant, and 37.9 mL of meadowfoam oil. The mixture was combined with AROMATIC 150 FLUID up to 3785 mL, and 600 ML of the resulting mixture was further mixed with 117 grams of iron naphthenate and 190 mL of iron pentacarbonyl. This formulation was prepared under normal atmospheric conditions with the iron naphthenate transferred anaerobically using a syringe. The iron content of the resulting solution was 6 wt. %. The residual fuel oil tested at IPT was additized with this additive at 813 ppm.

[00114] Table 14 shows particulate matter concentrations observed under treated and untreated conditions. The reduction in particulate matter is very significant at both 4.5% and 7% oxygen levels, but perhaps the more significant observation is that the particulate matter concentration observed under treated conditions for both the oxygen concentrations are very close. It is well known that under high excess oxygen combustion conditions, a significant fraction of the heat is lost to the flue gas. The tests showed that by shifting from 7.0% excess oxygen to about 4.5% excess oxygen, a 17% improvement in useful heat was realized. Using the fuel additive tested, this increase in efficiency was accompanied by a 43% decrease in particulate matter emissions.

Table 14. Particulate Emission at IPT Brazil

Excess O	Additive	Trial Number	Particulate Concentration (mg/Nm3)
7.0%	none	31	272
7.0%	none	32	301
7.0%	none	33	291
7.0%	none	42	289
7.0%	none	43	296
7.0%	yes	average	290
7.0%	yes	34	183
7.0%	yes	35	200
7.0%	yes	36	128
7.0%	yes	37	152
7.0%	yes	38	128
7.0%	yes	39	133
7.0%	yes	40	111
7.0%	yes	41	128
7.0%	yes	average	145
4.5%	none	57	415
4.5%	none	58	389
4.5%	none	59	415
4.5%	none	67	479
4.5%	none	68	504
4.5%	none	69	523
4.5%	none	average	454
4.5%	yes	60	163
4.5%	yes	61	166
4.5%	yes	62	160

4.5%	yes	63	162
4.5%	yes	65	173
4.5%	yes	66	169
4.5%	yes	average	166

[00115] Although the present invention and its advantages have been described in detail, it should be understood that various changes, substitutions and alterations can be made herein without departing from the spirit and scope of the invention as defined by the appended claims. Moreover, the scope of the present application is not intended to be limited to the particular embodiments of the process, machine, manufacture, composition of matter, means, methods and steps described in the specification. As one of ordinary skill in the art will readily appreciate from the disclosure of the present invention, processes, machines, manufacture, compositions of matter, means, methods, or steps, presently existing or later to be developed that perform substantially the same function or achieve substantially the same result as the corresponding embodiments described herein may be utilized according to the present invention. Accordingly, the appended claims are intended to include within their scope such processes, machines, manufacture, compositions of matter, means, methods, or steps.

WHAT IS CLAIMED IS:

1. A fuel additive for improving the combustion characteristics of a high-asphaltene carbonaceous fuel, the fuel additive comprising:

a plant extract; and

an organometallic compound.

2. The fuel additive of claim 1 wherein the plant extract is an extract of a plant from the *Leguminosae* family.

3. The fuel additive of claim 2 wherein the plant extract is selected from the group consisting of fescue extract, alfeque extract, alfalfa extract, and combinations thereof.

4. The fuel additive of claim 3 wherein the organometallic compound is a hydrocarbon-soluble organometallic compound containing at least one metal selected from the first and second row transition metals.

5. The fuel additive of claim 4 wherein the metal of the organometallic compound is iron

6. The fuel additive of claim 5 wherein the organometallic compound is selected from the group consisting of iron pentacarbonyl, iron naphthenate, ferrocene, and combinations thereof.

7. The fuel additive of claim 1 wherein the organometallic compound is a hydrocarbon-soluble organometallic compound containing at least one metal selected from the first and second row transition metals.

8. The fuel additive of claim 7 wherein the metal of the organometallic compound is iron

9. The fuel additive of claim 8 wherein the organometallic compound is selected from the group consisting of iron pentacarbonyl, iron naphthenate, ferrocene, and combinations thereof.

10. The fuel additive of claim 1 further comprising an oil-soluble carrier.

11. The fuel additive of claim 10 wherein the oil-soluble carrier is an aromatic solvent.

12. The fuel additive of claim 10 wherein the plant extract is provided in an amount from about 0.01 wt.% to about 10 wt.% of the fuel additive.

13. The fuel additive of claim 12 wherein the plant extract is provided in an amount from about 0.05 wt.% to about 5 wt.% of the fuel additive.

14. The fuel additive of claim 13 wherein the plant extract is provided in an amount of about 0.5 wt.% of the fuel additive.

15. The fuel additive of claim 1 further comprising a material selected from meadowfoam oil, a carotenoid, an anti-oxidant, and combinations thereof.

16. The fuel additive of claim 1 further comprising meadowfoam oil, a carotenoid, and an anti-oxidant.

17. The fuel additive of claim 16 wherein the carotenoid comprises β-carotene.

18. The fuel additive of claim 16 wherein the anti-oxidant comprises a dihydroquinoline.

19. The fuel additive of claim 18 wherein the dihydroquinoline comprises 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline.

20. The fuel additive of claim 1 wherein the plant extract is extracted by a hydrocarbon-soluble polar or nonpolar solvent.

21. A method of improving the combustion characteristics of a high-asphaltene carbonaceous fuel comprising adding a fuel additive to the high-asphaltene carbonaceous fuel, the fuel additive comprising:

a plant extract; and
an organometallic compound.

22. The method of claim 21 wherein the plant extract is an extract of a plant from the *Leguminosae* family.

23. The method of claim 22 wherein the plant extract is selected from the group consisting of fescue extract, alfeque extract, alfalfa extract, and combinations thereof.

24. The method of claim 23 wherein the organometallic compound is a hydrocarbon-soluble organometallic compound with a metal selected from the first and second row transition metals.

25. The method of claim 24 wherein the metal of the organometallic compound is iron.

26. The method of claim 25 wherein the organometallic compound is selected from the group consisting of iron pentacarbonyl, iron naphthenate, ferrocene, and combinations thereof.

27. The method of claim 21 wherein the organometallic compound is a hydrocarbon-soluble organometallic compound with a metal selected from the first and second row transition metals.

28. The method of claim 27 wherein the metal of the organometallic compound is iron.

29. The method of claim 28 wherein the organometallic compound is selected from the group consisting of iron pentacarbonyl, iron naphthenate, ferrocene, and combinations thereof.

30. The method of claim 21 wherein the fuel additive further comprises an oil-soluble carrier.

31. The method of claim 21 wherein the oil-soluble carrier is an aromatic solvent.

32. The method of claim 21 wherein the high-asphaltene carbonaceous fuel is selected from residual fuel oil and coal.

33. The method of claim 32 wherein the plant extract is provided in an amount from about 0.5 ppm to about 10,000 ppm of the amount of high-asphaltene carbonaceous fuel.

34. The method of claim 33 wherein the plant extract is provided in an amount from about 200 ppm to about 2000 ppm of the amount of high-asphaltene carbonaceous fuel.

35. The method of claim 34 wherein the plant extract is provided in an amount of about 800 ppm of the amount of high-asphaltene carbonaceous fuel.

36. The method of claim 21 wherein the fuel additive further comprises a material selected from meadowfoam oil, a carotenoid, an anti-oxidant, and combinations thereof.

37. The method of claim 21 wherein the fuel additive further comprises meadowfoam oil, a carotenoid, and an anti-oxidant.

38. The method of claim 37 wherein the carotenoid comprises β-carotene.

39. The method of claim 37 wherein the anti-oxidant comprises a dihydroquinoline.

40. The method of claim 39 wherein the dihydroquinoline comprises 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline.

41. The method of claim 21 wherein the plant extract is extracted by a hydrocarbon-soluble polar or nonpolar solvent.

42. A fuel comprising a high-asphaltene carbonaceous fuel and a fuel additive, the fuel additive comprising:

a plant extract; and
an organometallic compound.

43. The fuel of claim 42 wherein the plant extract is an extract of a plant from the *Leguminosae* family.

44. The fuel of claim 43 wherein the plant extract is selected from the group consisting of fescue extract, alfeque extract, alfalfa extract, and combinations thereof.

45. The fuel of claim 42 wherein the organometallic compound is a hydrocarbon-soluble organometallic compound with a metal selected from the first and second row transition metals.

46. The fuel of claim 45 wherein the organometallic compound is selected from the group consisting of iron pentacarbonyl, iron naphthenate, ferrocene, and combinations thereof.

47. The fuel of claim 42 wherein high-asphaltene carbonaceous fuel is selected from residual fuel oil and coal.

48. The fuel of claim 47 wherein the plant extract is provided in an amount from about 0.5 ppm to about 10,000 ppm of the high-asphaltene carbonaceous fuel.

49. The fuel of claim 48 wherein the plant extract is provided in an amount from about 200 ppm to about 2000 ppm of the high-asphaltene carbonaceous fuel.

50. The fuel of claim 49 wherein the plant extract is provided in an amount of about 800 ppm of the high-asphaltene carbonaceous fuel

51. The fuel of claim 42 further comprising a material selected from meadowfoam oil, a carotenoid, an anti-oxidant, and combinations thereof.

52. The fuel of claim 42 further comprising meadowfoam oil, a carotenoid, and an anti-oxidant.

53. The fuel of claim 52 wherein the carotenoid comprises β-carotene.

54. The fuel of claim 52 wherein the anti-oxidant comprises a dihydroquinoline.

55. The fuel of claim 54 wherein the dihydroquinoline comprises 2,2,4-trimethyl-6-ethoxy-1,2-dihydroquinoline.

56. The fuel of claim 42 wherein the plant extract is extracted by a hydrocarbon-soluble polar or nonpolar solvent.

FIG. 1

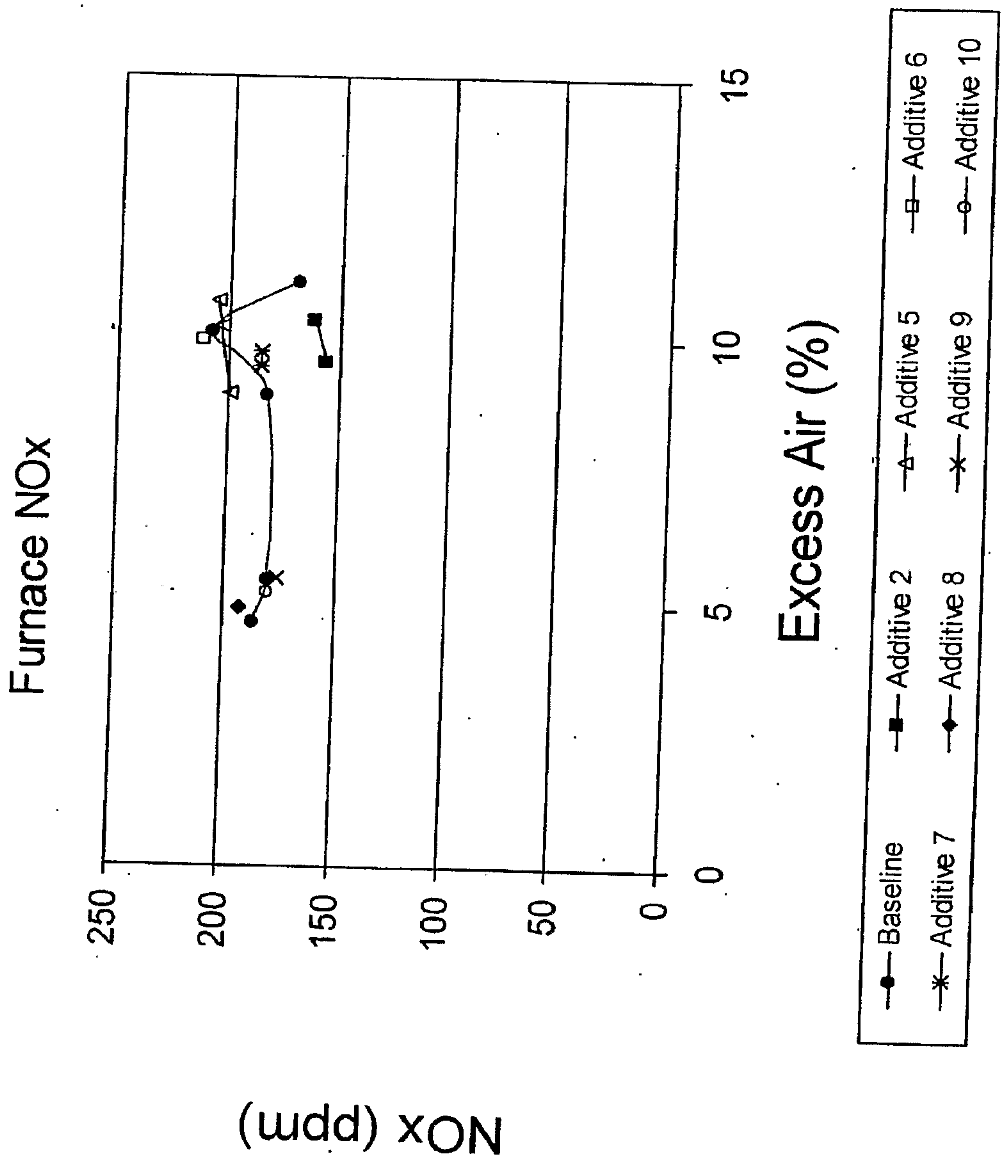

Furnace NOx
NOx (ppm)
250
200
150
100
50
0
0
5
10
15
Excess Air (%)
Baseline
Additive 2
Additive 5
Additive 6
Additive 7
Additive 8
Additive 9
Additive 10

FIG. 2

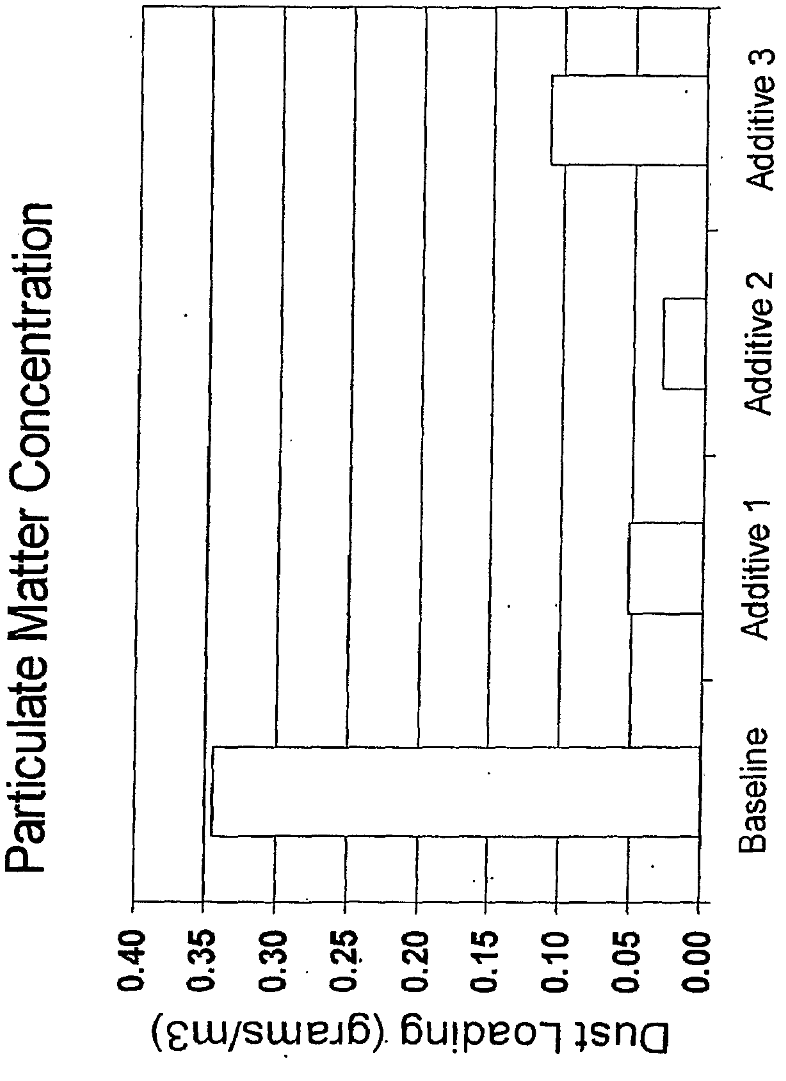

Particulate Matter Concentration
Dust Loading (grams/m3)
0.40
0.35
0.30
0.25
0.20
0.15
0.10
0.05
0.00
Baseline
Additive 1
Additive 2
Additive 3

FIG. 3

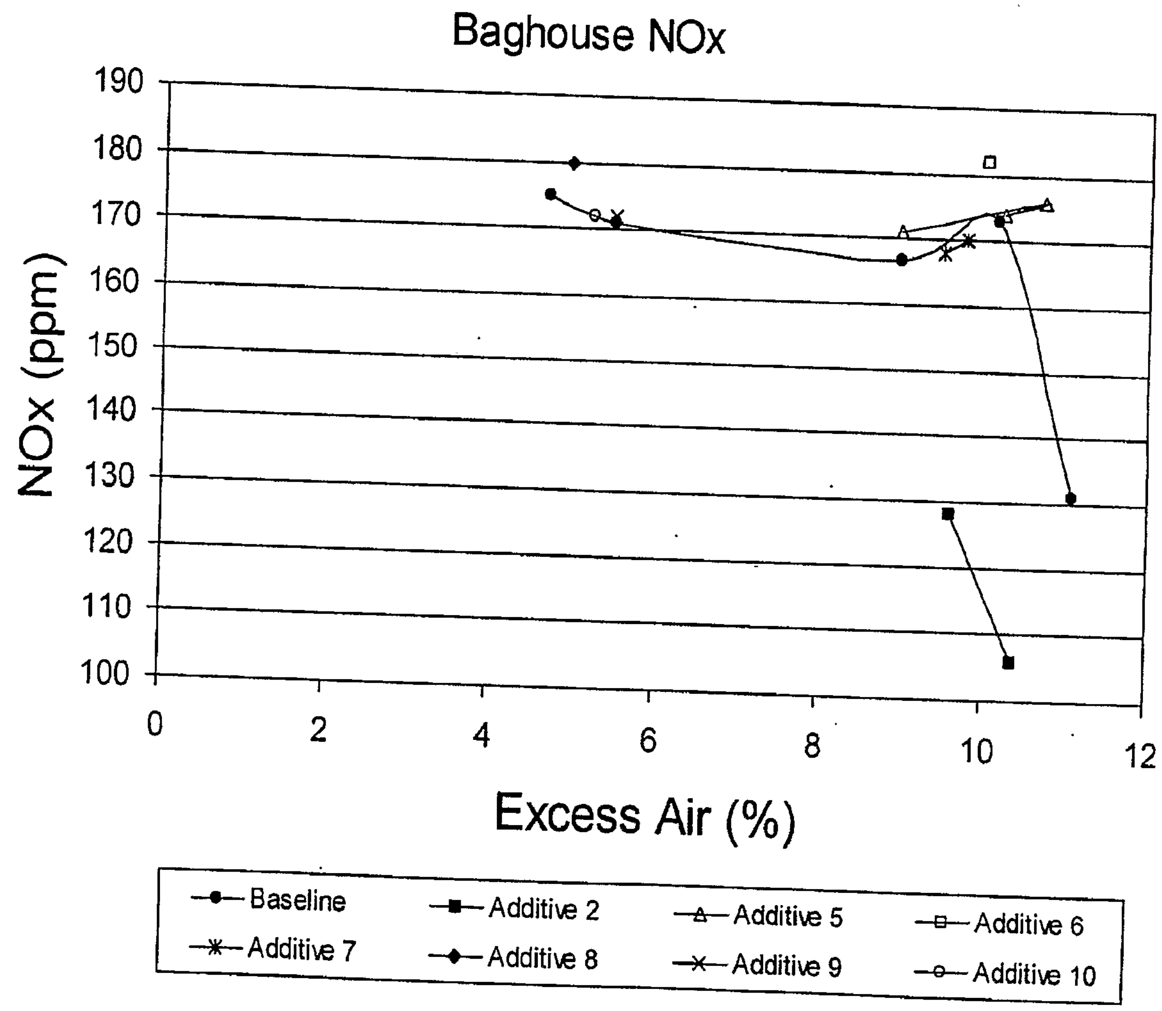

Baghouse NOx
NOx (ppm)
190
180
170
160
150
140
130
120
110
100
0
2
4
6
8
10
12
Excess Air (%)
Baseline
Additive 2
Additive 5
Additive 6
Additive 7
Additive 8
Additive 9
Additive 10

FIG. 4

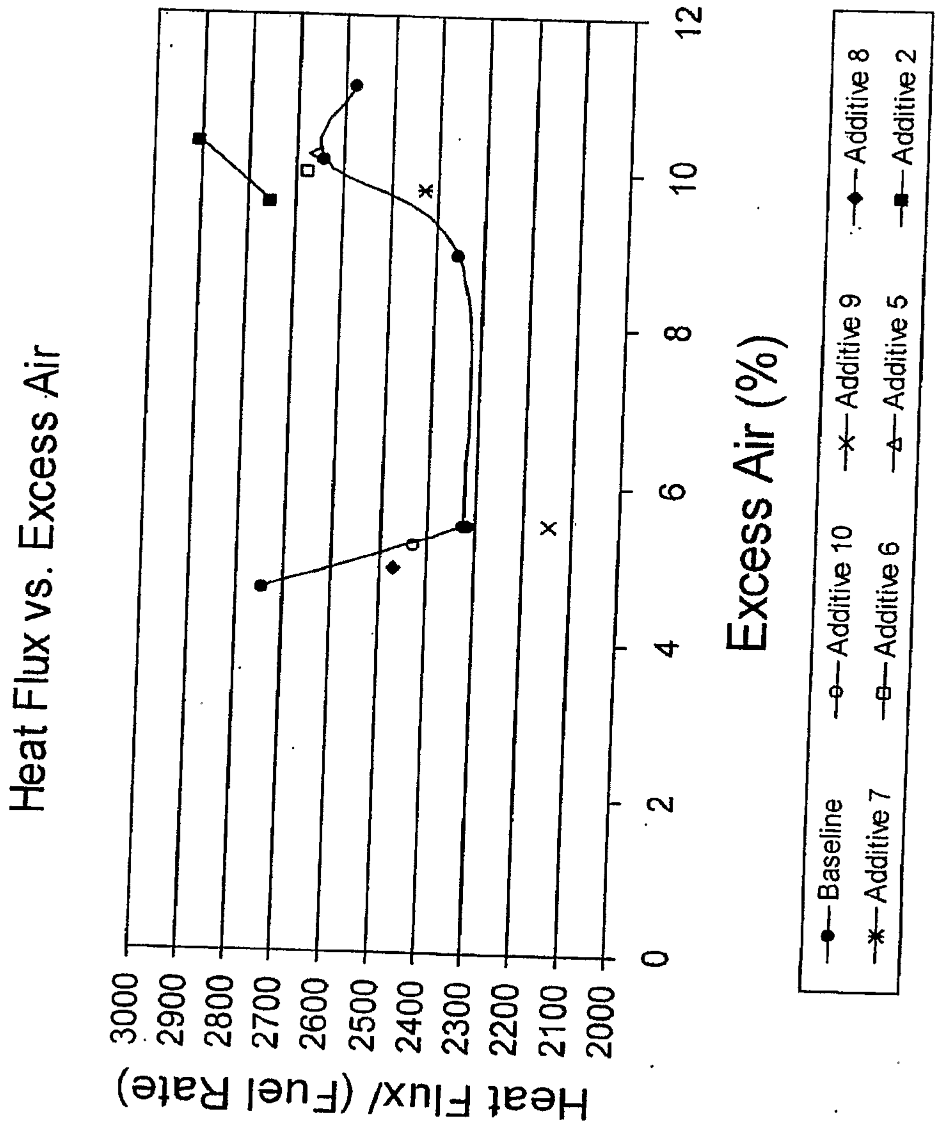
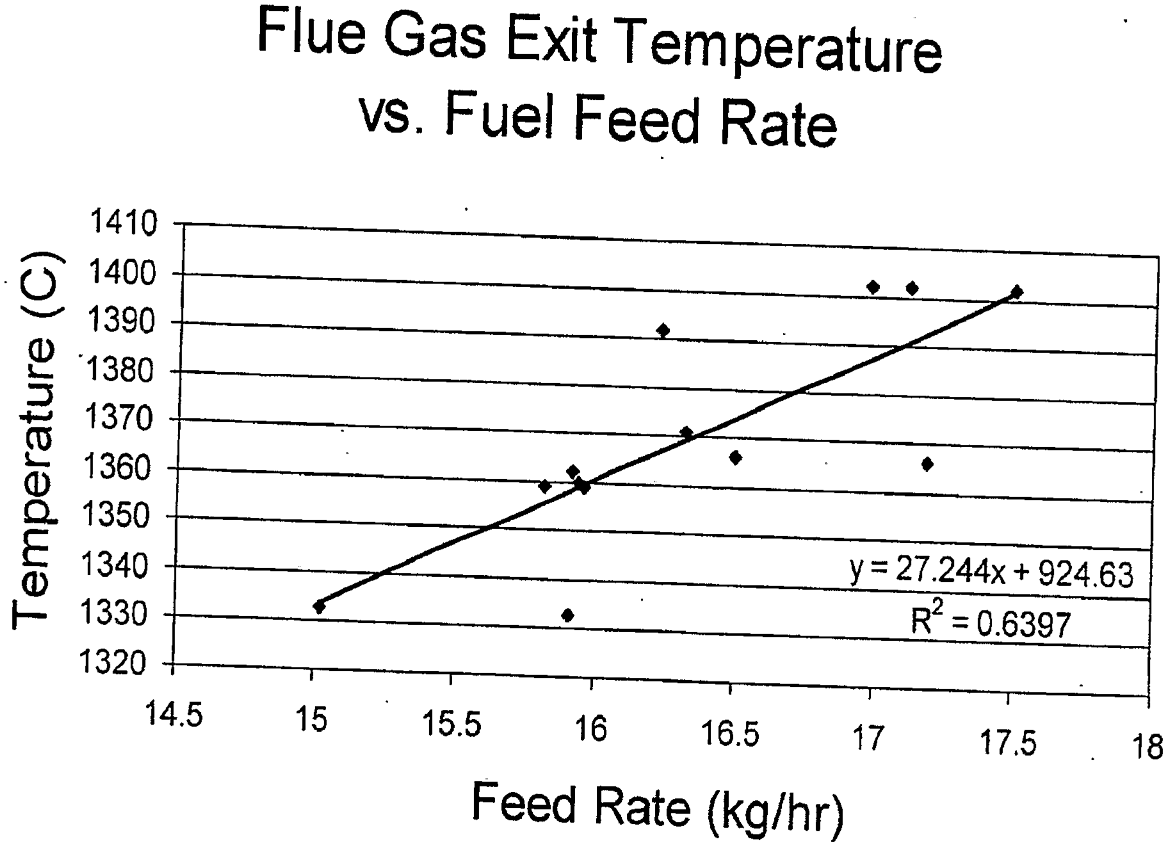

Heat Flux vs. Excess Air
Heat Flux/ (Fuel Rate)
3000
2900
2800
2700
2600
2500
2400
2300
2200
2100
2000
0
2
4
6
8
10
12
Excess Air (%)
Baseline
Additive 10
Additive 9
Additive 8
Additive 7
Additive 6
Additive 5
Additive 2

FIG. 5


Flue Gas Exit Temperature
vs. Fuel Feed Rate
Temperature (C)
1410
1400
1390
1380
1370
1360
1350
1340
1330
1320
14.5
15
15.5
16
16.5
17
17.5
18
Feed Rate (kg/hr)
y = 27.244x + 924.63
R2 = 0.6397