Example of Production of a Pyrolysis Oil Based Fuel

Assume producing 1,000 kilograms of pyrolysis oil based biofuel

Operative conditions:
- T = 20°F to 100°F
- P = 1 atm

- m_{\text{pyrolysis oil}} = 728.0 kg
- m_{\text{ULSD}} = 1.0 kg
- m_{\text{Hypermer 1080}} = 8.5 kg
- m_{\text{incromide}} = 2.5 kg

740 kg mixed
Through IKA unit
818 kg mixed

182 kg

Second Water/ \text{C}_2\text{H}_4\text{O}_2
Batch

- m_{\text{H}_2\text{O}} = 133 kg
- m_{\text{C}_2\text{H}_4\text{O}_2} = 49 kg

1000 kg mixed
Example of Production of a Pyrolysis Oil Based Fuel

Assume producing 1,000 kilograms of pyrolysis oil based biofuel.

\[
\text{m}_{\text{Pyrolysis oil}} = 728.0 \text{ kg}
\]

\[
\text{m}_{\text{#2 } \text{ ULSD}} = 1.0 \text{ kg}
\]

\[
\text{m}_{\text{Hypermer 090}} = 8.5 \text{ kg}
\]

\[
\text{m}_{\text{Inconel}} = 2.5 \text{ kg}
\]

Operative conditions:
\[T = 20 \text{ F} \text{ to } 100 \text{ F}
\]
\[P = 1 \text{ atm}
\]

\[\text{m}_{\text{H}_2\text{O}} = 57 \text{ kg}
\]

\[\text{m}_{\text{C}_2\text{H}_6\text{O}_2} = 21 \text{ kg}
\]

\[\text{m}_{\text{H}_2\text{O}} = 133 \text{ kg}
\]

\[\text{m}_{\text{C}_2\text{H}_6\text{O}_2} = 49 \text{ kg}
\]

\[\text{740 kg mixed through IKA unit}
\]

\[818 \text{ kg mixed}
\]

\[\text{Output to Holding Tank or Transport Tank Fuel}
\]

\[\text{1,000 kg}
\]
PYROLYSIS OIL BASED FUEL AND METHOD OF PRODUCTION

PRIORITY
[0001] This application claims priority to U.S. provisional patent application Ser. No. 61/361,771 filed Jul. 6, 2010 entitled PYROLYSIS OIL BASED FUEL AND METHOD OF PRODUCTION, the disclosure of which is hereby incorporated by reference in the entirety.

TECHNICAL FIELD

[0002] Embodiments of the invention related generally to alternative fuels and methods of producing alternative fuels, and more specifically to alternative fuels based on pyrolysis oil.

BACKGROUND OF THE INVENTION

[0003] Efforts to find alternative fuels to those derived from petroleum, such as gasoline and diesel fuel, have led to the development of various biomass based fuels. One potential biomass based fuel source is pyrolysis oil, which is an oil or tar product produced by the pyrolysis of biomass materials such as wood, agricultural waste, and municipal waste, as well as non-biomass materials.

[0004] Pyrolysis oil presents an attractive source of renewable energy. It has been considered as a potential substitute for petroleum, or for use in a blend with petroleum, as a renewable source of energy. Furthermore, there are many well known and well developed processes for producing pyrolysis oil, and the source materials which may be used for the production of pyrolysis oil are diverse and abundant. However, the physical characteristics of pyrolysis oil have, so far, limited the usefulness and commercial development of pyrolysis oil based fuel as a replacement for petroleum or for use in blending with petroleum.

[0005] Crude pyrolysis oil has numerous problems that limit its usefulness in petroleum powered engines and other systems. Pyrolysis oil experiences an increase in viscosity over time. Although hydrocarbons also become viscous over time, the increase in viscosity occurs much more quickly for pyrolysis oils. Attempts have been made to treat this viscosity problem using a thermal catalytic cracking process at the end of production of the oil (viscosity breaking). However, this results in a cost increase and does not completely resolve the problem of polymerization over time. In addition, pyrolysis oils undergo phase changes over time which can result in the separation of the oil into multiple phases including water, wax, sludge, and tar. Pyrolysis oil does not revaporize following a distillation curve, like hydrocarbons do. Rather, when pyrolysis oil is heated, volatiles and water vaporize and the remaining compounds polymerize. In addition, the pH of pyrolysis oils is very low. Past efforts to increase the pH by adding base compounds to the pyrolysis oil have been unsuccessful. The treated pyrolysis oil is unstable, such that over time the salts precipitate out. In addition, this treatment adds costs and contaminants to that can lead to polymerization or leaking of the nozzles of turbines and engines. Finally, pyrolysis oil does not mix well with hydrocarbons.

SUMMARY OF THE INVENTION

[0006] Embodiments of the invention include fuel compositions including pyrolysis oil, water, and surfactant. Some embodiments further include one or more alcohols. The pyrolysis oil fuels are stable emulsions that may be used as replacements for, or may be mixed with, fossil fuels such as diesel and gasoline.

[0007] In some embodiments, the fuel composition is an emulsion including 50-90 wt % pyrolysis oil, 0.1-40 wt % water, 1-30 wt % alcohol, and 0.1-4 wt % surfactant. The pyrolysis oil comprises crude pyrolysis oil, which may be derived from biomass such as wood or other lignocellulosic materials, or from non-biomass sources. In some embodiments, the fuel composition optionally includes diesel fuel. The pyrolysis oil and surfactant may form the continuous phase and the water and alcohol may form the dispersed phase of the emulsion. Alternatively, the water and alcohol may form the continuous phase and the pyrolysis oil and surfactant form the dispersed phase of the emulsion.

[0008] In some embodiments, the alcohol includes one or more polyalcohols or glycols. In some embodiments, the alcohol comprises propylene glycol, ethylene glycol and/or ethanol.

[0009] In some embodiments, the surfactant includes a non-ionic polymeric surfactant, such as Hypermer 1083SF, Monoamine ADD, or Incromide. In some embodiments, the surfactant includes Chemax EM-1160. In other embodiments, the surfactant includes Tween 80. In some embodiments, the composition also includes a co-surfactant. In some embodiments, the surfactant is Hypermer 1083SF and the co-surfactant is Monoamine ADD or Incromide. In other embodiments, the surfactant is Chemax EM-1160 and the co-surfactant is Tween 80.

[0010] Other embodiments of the invention include a first phase comprising water and alcohol and a second phase comprising pyrolysis oil and surfactant. Either the first or the second phase forms a continuous phase and the other of the first and second phases forms a dispersed phase.

[0011] Embodiments of the invention also include a method of forming a stable pyrolysis oil based fuel emulsion. In some embodiments, the method includes combining water and alcohol to form a water and alcohol mixture, separately combining pyrolysis oil and a surfactant to form a pyrolysis oil and surfactant mixture, adding a first portion of the water and alcohol mixture to the pyrolysis oil and surfactant mixture, and mixing until a stable emulsion is formed. In some embodiments, the first and second portions of the water and alcohol mixture are formed together when the water and alcohol mixture is mixed, and then divided into the first and second portions. In other embodiments, the first and second portions of the water and alcohol mixture are made separately by combining a first quantity of water and a first quantity of alcohol to form the first portion and by combining a second quantity of water and a second quantity of alcohol to form the second portion.

[0012] In other embodiments, the method of forming a stable pyrolysis oil based fuel emulsion includes combining water and alcohol to form a water and alcohol mixture, separately combining pyrolysis oil and a surfactant to form a pyrolysis oil and surfactant mixture, adding a first portion of the pyrolysis oil and surfactant mixture to the water and alcohol mixture and mixing, adding a second portion of the pyrolysis oil and surfactant mixture to the water and alcohol mixture, and mixing until a stable emulsion is formed. As described above, the first and second portions of the pyrolysis...
oil and surfactant mixture may be made together and then separated into separate portions or the portions may be made separately.

FIGURES

[0013] FIG. 1 is a flow chart showing an exemplary process for the production of a pyrolysis oil based fuel according to embodiments of the invention.

DETAILED DESCRIPTION

[0014] Embodiments of the invention include pyrolysis oil based fuels, also referred to interchangeably as pyrolysis oil fuels, and methods of making pyrolysis oil based fuels using an emulsification process. The pyrolysis oil fuels are renewable fuels which may be used to replace distillate oil for power generation, electricity, and diesel generators, for example. The pyrolysis oil fuel may also be co-fired with coal and/or biomass. Furthermore, it avoids complicated biofuel processes such as transesterifications used for traditional biodiesel but rather can be produced using a simple emulsification process.

[0015] The pyrolysis oil fuel includes pyrolysis oil, water, and emulsifiers and typically includes one or more alcohols. However, in some embodiments, the alcohol may be optional. It may also include other optional components including additives such as combustibles. In some embodiments, the pyrolysis oil fuel composition may be used as a neat biofuel. In some embodiments, the pyrolysis oil fuel includes a petroleum fuel such as diesel. In other embodiments, the pyrolysis oil fuel may be blended with a fossil fuel such as diesel and/or gasoline or with a non-fossil fuel such as biodiesel or bioethanol.

[0016] In one embodiment, the pyrolysis oil fuel includes about 50-95 wt % pyrolysis oil from one or more biomass sources, about 0.1-40 wt % water, about 1-30 wt % alcohol and/or polyalcohol, about 0.01-4 wt % surfactant. In some embodiments, the pyrolysis oil fuel further includes about 0.01-4 wt % co-surfactant or stabilizer. Some embodiments may also include about 0.01-15 wt % diesel fuel. In some embodiments, the surfactant and/or co-surfactant are non-ionic polymeric surfactants.

[0017] Embodiments of the invention may be formed as emulsions. The term emulsion refers to a mixture or dispersion of two immiscible substances, liquids in the present invention, in which one substance, the dispersed phase, is dispersed in the other substance, the continuous phase. The emulsion is stabilized, in other words the dispersed phase remains dispersed during the relevant time period, such as during storage and/or immediately prior to and during use, with the assistance of one or more emulsifiers.

[0018] The pyrolysis oil fuel emulsions include water-in-oil emulsions, having pyrolysis oil as the continuous phase. Alternatively, the pyrolysis oil fuel emulsions may be oil-in-water emulsions, having water as the continuous phase. The type of emulsion formed may depend upon such variables as the amounts of pyrolysis oil and water present, the conditions used to prepare the emulsion, the emulsifier type and amount, the temperature and combinations of such variables. The emulsions are stable, with the dispersed phase remaining substantially dispersed in the continuous phase. In other words, substantially no phase separation occurs as indicated by visual observation after a period following preparation of the emulsion of at least about 24 hours; such as at least about 48 hours or at least about 72 hours. In some embodiments, substantially no phase separation is observable after about 4 days or more, at ambient temperatures suitable for use of the emulsified fuel composition in its intended application, for example use in burners, motor vehicles and the like.

[0019] In one embodiment, the pyrolysis oil fuel include about 50-95 wt % pyrolysis oil, about 0.1-40 wt % water, about 0-30 wt % alcohol, about 0.01-4 wt % Hypermer® 1083SF, about 0.01-4 wt % MONOAMINE™ ADD-100 (Incomride), and about 0-15 wt % #2 Diesel. In some embodiments, the alcohol includes one or more of propylene glycol, ethylene glycol, and ethanol.

[0020] In another embodiment, the pyrolysis oil fuel includes 50-95 wt % pyrolysis oil, 0.1-40 wt % water, 0-30 wt % ethylene glycol, 0-30 wt % propylene glycol, 0.01-4 wt % Chemax EM-1169, 0.01-4 wt % Tween 80, and 0-15 wt % Diesel fuel, such as #2 Diesel fuel.

[0021] Pyrolysis oil fuel compositions described herein are suitable for use in internal combustion engines, including diesel engines of various configurations, as well as in equipment that combusts fuels to generate heat, such as furnaces, boilers, power generating equipment and the like, including gas or combustion turbines. Diesel engines that may be operated with compositions of the present invention include all compression-ignition engines for both mobile (including locomotive and marine) and stationary power plants. These include diesel engines of the two-stroke-per-cycle and four-stroke-per-cycle types. The diesel engines, include but are not limited to light and heavy duty diesel engines and on and off-highway engines, including new engines as well as in-use engines. The diesel engines include those used in automobiles, trucks, buses including urban buses, locomotives, stationary generators, and the like. For example, with regard to use in burners, the compositions are useful in different types of oil burners for domestic and other heating purposes including sleeve burners, natural-draft pot burners, force-draft pot burners, rotary wall flame burners, and air-mistizing and pressure-mistizing gun burners; with the latter type of burner being the most commonly used burner for home heating, particularly in the United States. In particular, such compositions are useful fuels for diesel motors (both new and old generation) and/or boilers and single- or multi-step burners, also referred to in the art as staged burners.

[0022] Product and manufacturing costs for the pyrolysis oil fuels are low and competitive with other fuels, particularly due to the presence of water in the composition. In addition, some embodiments of the fuel of the invention are renewable since they are based on pyrolysis oil obtained from plant material that can be regularly replaced. Furthermore, the pyrolysis oil biofuels according to embodiments of the invention exhibit substantial improvement in physical characteristics as compared to pyrolysis oil.

[0023] The pyrolysis oil fuels according to embodiments of the invention have a higher flash point than crude pyrolysis oil. The term flash point generally refers to how easily a substance or composition, typically a fluid, may ignite or burn and is one property that needs to be considered in determining the suitability of a fuel composition for practical use. Materials with higher flash points are less likely to ignite than those with lower flash points. Crude pyrolysis oil has a flash point of <38°C (<100°F) or 38-100°C and is not auto-igniting in a diesel engine. In contrast, the flash point of the pyrolysis oil fuels disclosed herein have a flash point of >99°C (>210°F). This flash point allows the pyrolysis oil fuel to be classified as
a combustible rather than a flammable, like crude pyrolysis oil. This results in cost savings related to permitting and storage issues in a production plant, because less mandatory safety equipment is required for combustibles and the management of health and safety issues is less complicated. The higher flash point also allows for use in more markets, such as marine combustion engines and motors, which have a mandatory flash point of greater than 140°F.

[0024] The viscosity of crude pyrolysis oil is about 60 to 300 cSt at 40°C, and increases further over time, such as over a period of 12 months, due to polymerization. The viscosity of the present biofuels based on pyrolysis oil improves to a value of less than 10 cSt at 40°C, such as 3-5 cSt. At this level, the biofuel is compliant with GE Gas Turbine Fuel Specification (GEI 41047) for high pressure air atomizing system. It is also within the viscosity range of diesel fuel, which is about 3-5 cSt at 40°C.

[0025] The pour point of crude pyrolysis oil is about 4°C to ~12°C, indicating that it may gel at or below those temperatures. In contrast, the pour point of the present pyrolysis oil fuels is enhanced to a maximum of ~24°C and a minimum of ~60°C. At this pour point, the biofuel is suitable for use in very low temperature and severe cold weather conditions.

[0026] The pH of the pyrolysis oil fuel is increased from about 1.5-3.8 in crude pyrolysis oil to greater than about 5 in some embodiments. In other embodiments, the pH of the pyrolysis oil fuel is greater than 6 or greater than 7. At these pH levels, the corrosive properties of the pyrolysis oil are reduced or eliminated.

[0027] Pyrolysis Oil is polar, due to the large amount of oxygenated compounds that it contains. This prevents the oil from readily mixing with hydrocarbons. However, the pyrolysis oil fuel as disclosed herein is blendable with distillate fuels such as diesel fuel.

[0028] The cetane number of pyrolysis oil is generally low, only approximately 10, and is not auto-igniting in a diesel engine. The cetane number, or CN, refers to a measure of diesel fuel ignition characteristics, with higher values indicating better performance. The cetane number scale covers the range from zero to 100, but typical test results for diesel fuel and fuels intended for use in diesel applications are in the range of about 30 to 65 cetane number. The cetane number measures how quickly the fuel starts to burn (auto-ignites) under a standardized set of diesel engine conditions. The pyrolysis oil fuels according to embodiments of the invention may have a cetane number greater than 10, due to the presence of polyalcohols and/or glycols. For example, nitrate alcohol esters such as tetraethyl glycol dinitrate may enhance the cetane number of the crude pyrolysis oil.

[0029] Pyrolysis oil is not stable, reacting with air and degassing. In contrast, the pyrolysis oil fuel compositions remain stable.

[0030] The pyrolysis oil fuels are emulsions that are stable for an extended time and over a wide range of temperatures. It can be used without modification to the tanks and/or piping systems of the motors and burners in common use. Thus another advantage of the present invention is that it permits the return at any moment to the use of traditional fuels without modification of the systems in which the fuel is used.

[0031] Crude pyrolysis oil cannot be blended with diesel. In contrast, the pyrolysis oil compositions blend well with diesel or other distillate fuels such as gasoline.

[0032] The combustion of crude pyrolysis oil results in the emission of high levels of SOx and NOx. In addition, the crude pyrolysis oil has a tendency to create coking at the injectors or nozzles of diesel engines. While sulfur can be removed from crude pyrolysis oil by processes such as catalytic post combustion of emissions (including selective non-catalytic reduction, SNCR, and selective catalytic reduction, SCR), these processes are expensive. In addition, the presence of high levels of alkaline metals can disrupt the catalyst used in SCR. In the pyrolysis oil fuel compositions described herein, the presence of water and alcohol in the emission reduces the NOx emissions and, together with the alcohols, dilutes the sulfur content. In addition to reducing emissions after combustion of the pyrolysis oil fuel, it also reduces or prevents clogging of the nozzles or injectors as would occur with the combustion of crude pyrolysis oil.

[0033] The presence of alcohols and/or polyalcohols in the pyrolysis oil fuel increases the energy content of the biofuel, recovering the heat loss of water. The quantity of alcohols and polyalcohols can be used in the pyrolysis oil fuel can therefore be adjusted relative to the quantity of water such that the energy increase due to the alcohols and polyalcohols can balance the lack of energy contribution from the water.

Pyrolysis Oil

[0034] The fuels useful in the present invention are based on pyrolysis oil, which is liquid fuel product produced by the pyrolysis of biomass or other materials and subsequent cooling. Pyrolysis oil is also known as, and/or includes, biomass pyrolysis oil, bio-oil, wood pyrolysis oil, wood oil, liquid wood, biomass pyrolysis liquid, bio-crude oil, or pyrolygenous tar. Alternately, pyrolysis oil may be obtained from non-biomass sources such as rubber tires and plastics. Pyrolysis oil is a synthetic fuel extracted by means of destructive distillation, forming a kind of tar which normally contains oxygen at levels which are too high for it to be defined as a hydrocarbon. Pyrolysis oil may form about 50-95 wt % of the fuel. In some embodiments, it is about 60-85 wt % of the fuel, and in other embodiments it is about 70-75 wt % of the fuel.

[0035] Biomass pyrolysis for the production of pyrolysis oil may use any biomass substrate. For example, the biomass substrate may be hard or soft woody plants including trees and bushes, non-woody plants, agricultural materials or waste, grasses, municipal waste, or a combination of one or more biomass materials. Examples of woody plant material which may be used include trees such as pine, poplar, birch, willow, fir, spruce, larch, beech, and palm. Examples of agricultural materials and wastes include bagasse, corn, corn stover, corn cobs, corn kernels, corn fibers, straw (rice, oat, wheat, barely, canola), hulls (rice, oat), soybean stover, cotton stalk, cotton gin, sugar cane, sugar bagasse, and sugar processing residues. Examples of grasses which may be used include switchgrass, miscanthus, sorghum, cordgrass, ryegrass, Bermuda grass, reed canary grass, and alfalfa. Municipal waste includes waste paper and food and industrial waste such as paper and other waste.

[0036] Biomass pyrolysis for the production of pyrolysis oil is performed using a very high heating rate as well as a high heat flux. Under these conditions, the chemical bonds of the cellulose, hemicellulose and lignin components of the biomass are cleaved, producing a vapor, a gas and char. The vapor is then thermally quenched to prevent further cracking and to produce pyrolysis oil.

[0037] Alternatively, pyrolysis oil may be produced from waste products such as tires, plastic scraps and car fluff. Pyrolysis oil which is derived from non-biomass sources may
contain more contaminants, such as sulphur, and may have a higher btu content than pyrolysis oil derived from biomass sources. Non-biomass sources of pyrolysis oil include plastic, such as post consumer plastic (PCP), which is often mixed with other urban solid waste, and other solid rubbish.

Pyrolysis oil may be produced by either fast pyrolysis or slow pyrolysis, though fast pyrolysis may produce a greater yield of pyrolysis oil. Generally, the biomass is exposed to temperatures about 320-500°C, followed by cooling. Various reactor systems may be used for biomass pyrolysis. These reactors can apply pyrolysis conditions to the biomass using fluidized beds (bubbling or circulating), transported beds, circulating fluid beds, ablative sources (vortex and rotating blades), vacuums, transported beds without a carrier gas, grate kilns, microwave inputs, or rotating cones, for example.

The exact characteristics and composition of the pyrolysis oil will vary somewhat depending upon the method of pyrolysis performed and the nature of the biomass feedstock. Pyrolysis oil is typically a mixture of a large number of compounds that are fragments of the original biomass component, including a large amount of oxygenated compounds. Pyrolysis oil includes organic acids such as formic and acetic acid, resulting in the low pH of about 1.5-3.8. It is also polar and hydrophobic, and may have an oxygen content of about 40-50%. It has a density of approximately 1.2-1.3 kg/l or 10.01-10.85 lbs/gallon, which is higher than that of diesel.

Crude pyrolysis oil may include lignin. However, embodiments of the invention can produce pyrolysis oil based fuel with or without removal of the lignin from the crude pyrolysis oil. Crude pyrolysis oil may also have a water content which can vary from 1-30%, for example. This water may have been split during pyrolysis and may be held separately in other compounds within the complex pyrolysis liquid. While the water can be removed from the crude pyrolysis oil, it is an expensive process, and embodiments of the invention do not require removal of the water from the crude pyrolysis oil. Rather, the amount of water present in the crude pyrolysis oil can be used to form a portion or all of the water content of the final pyrolysis oil based fuel. For example, the water content of the crude pyrolysis oil to be used for the fuel production can be measured. Based on the amount of crude pyrolysis oil to be used, the contribution of this water content to the total amount of water in the fuel can be calculated. The amount of water to be added to the fuel can be adjusted down by this amount, to reach the final desired total water content.

Water

The water used in the compositions of the present invention can be from any source. The water employed in preparing the pyrolysis oil fuel compositions of the present invention can be deionized, purified for example using reverse osmosis or distillation, and/or demineralized and have a low content of dissolved minerals, for example, salts of calcium, sodium and magnesium, and will similarly include little, if any, chlorine and/or fluorine as well as being substantially free of undissolved particulate matter. In some embodiments, the water has been substantially demineralized by methods well known to those skilled in the art of water treatment in order to remove dissolved mineral salts and has also been treated to remove other additives or chemicals, including chlorine and fluorine. The substantial absence of such materials may lead to improvements in the condition of metal surfaces in engines and burners, particularly the inner surfaces of cylinders and nozzles. Some or all of the water present in the composition may be provided as water present in the crude pyrolysis oil, so that refining of the crude pyrolysis oil may be avoided. The water may be present in the pyrolysis oil fuel emissions at amounts of about 0.1% to about 40% by weight; alternatively about 5% to about 40% by weight; about 10% to about 30% by weight; or about 15% to about 25%.

Emulsifiers

Emulsifiers used in embodiments of the invention add stability in the pyrolysis oil fuel and can increase the blendability of the pyrolysis oil fuel with distillate fuels. The term emulsifier refers to a compound or mixture of compounds that has the capacity to promote formation of an emulsion and/or substantially stabilize an emulsion, at least for the short-term, i.e., during the time of practical or commercial interest. An emulsifier provides stability against significant or substantial aggregation or coalescence of the dispersed phase of an emulsion. An emulsifier is typically considered to be a surface active substance in that it is capable of interacting with the dispersed and continuous phases of an emulsion at the interface between the two. Surfactants are one type of emulsifier. Within the generic term surfactant are included various types of surfactants such as nonionic, ionic or partially ionic, anionic, amphoteric, cationic and zwitterionic surfactants.

Emulsifiers such as surfactants may be employed in accordance with the present invention to enhance the stability of the pyrolysis oil fuel emulsion, particularly over time. The following tabulation provides examples of surfactants contemplated by the invention, although useful surfactants are not limited to those specifically listed. For example, also useful are surfactants disclosed in a comprehensive listing of surfactants that can be found in the spectral database of Bio-Rad Laboratories (www.informatics.bio-rad.com), including infrared spectra and, in a number of cases, chemical composition and chemical and physical properties and sources, incorporated herein by reference. The compounds are generally characterized as alcohols, nitrogen-containing compounds, esters of long chain carboxylic acids, hydrocarbons, various esters and salts of long chain carboxylic acids, sulfated and sulfonated compounds including alkylaryl sulfonates, isothioniates, lignosulfonates, sulfated and sulfonated alcohols, amines, amides, carboxylic acids, carboxylic acid esters, sulfated and sulfonated polyalkoxylated materials such as esters, ethers, nitrogen compounds, aminopolyoxycarboxylic acids such as ethylenediaminetetraacetic acid (EDTA), diethylenetriaminepentaacetic acid (DTPA), and nitrioltriacetic acid (NTA), in other words EDTA, DTPA, NTA acids and salts, phosphates, silicates and siliccones. To the extent that a particular surfactant includes atoms, groups or compounds that may unnecessarily contribute to pollution, e.g., sulfur, its use can be limited to the amount necessary for producing and/or maintaining a stable emulsion or fuel composition. In some embodiments, the surfactant may be cetyl alcohol, hydrogenated castor oil or a mixture of cetyl alcohol and hydrogenated castor oil. The following materials, referred to as surfactants herein, can be employed in accordance with the pyrolysis oil fuel compositions of the present invention.

In some embodiments, the surfactant is a fatty amine, ethanol amide or alkoxylated amide, such as those
available from Croda Inc. of Edison, N.J. under the trade-names Cromidet™, Incromectant™, Incromide™, and Promidium™, such as Incromide™ CDEA and Incromide™ LDEA.

[0045] Tabulation of Useful Surfactants

[0046] (A) Nonionic Surfactants:
Esters of polyhydric alcohols; alkoxylated amides; esters of polycarboxylic acids; polyoxypropylene and of polyoxyethylene-polyoxypropylene glycols; ethers of polycarboxylic acids; terciary acetylenic glycols; and polyoxyethylated alkyl phosphates. Particularly useful nonionic surfactants include Hypermer® 10835, a nonionic surfactant blend, and MONAMINE™ ADD-100 (cocamide DEA and Diéthanolamine), one of a range of alkylamidines known as Incromide™ CDEA. Both Hypermer® 10835 and MONAMINE™ ADD-100 are available from Croda Inc. of Edison, N.J.

[0047] (B) Anionic Surfactants:
Carboxylic acids and soaps; sulfated esters, amides, alcohols, ethers and carboxylic acids (all salts); sulfonated petroleum, aromatic hydrocarbons, aliphatic hydrocarbons, esters, amides, amines, ethers, carboxylic acids, and lignins (all salts); acylated polypeptides (salts); and phosphates.

[0048] (C) Fatty Acids:
Caprylic acid, abietic acid, pelargonic acid, coconut oil fatty acids, capric acid, corn oil fatty acids, lauric acid, cottonseed oil fatty acids, myristic acid, soybean oil fatty acids, palmitic acid, tallow fatty acids, stearic acid, hydrogenated fish oil fatty acids, behenic acid, tall oil fatty acids, undecylenic acid, dimer acids, oleic acid, trimer acids, erucic acid, castor oil, linoleic acid, hydrogenated castor oil, ricinoleic acid, lanolin, naphthenic acid, and lanolin fatty acids.

[0049] (D) Fatty Acid Salts:
Lithium stearate, ammonium oleate, cadmium stearate, sodium caprate, ammonium linoleate, calcium stearate, sodium laurate, ammonium ricinoleate calcium oleate, sodium myristate, ammonium naphthenates, calcium linoleate, sodium palmitate, ammonium abietate, calcium ricinoleate, sodium stearate, morpable linoleate, calcium naphthenates, sodium undecylenate, morphine myristate, cobalt stearate, sodium oleate, morpholine palmitate, cobalt naphthenates, sodium linoleate, morpholine stearate, copper stearate, sodium ricinoleate, morpholine undecylenate, copper oleate, sodium naphthenates, morpholine oleate, copper naphthenates, sodium abiate, morpholine linoleate, iron stearate, sodium polymerized carboxylates, morpholine ricinoleate, triolabpropionate, morpholine naphthenate, lead stearate, sodium salt of tall oil, morpholine abiate, lead oleate, potassium caprate, triethanolamine caprate, lead naphthenate, potassium laurate, triethanolamine laurate, magnesium stearate, potassium myristate, triethanolamine myristate, magnesium oleate, potassium palmitate, magnesium stearate, potassium undecylenate, triethanolamine stearate, nickel oleate, potassium oleate, strontium stearate, potassium linoleate, triethanolamine undecylenate, tin oleate, potassium ricinoleate, zinc laurate, potassium naphthenate, triethanolamine oleate, zinc palmitate, potassium abiate, triethanolamine linoleate, zinc stearete, ammonium caprate, triethanolamine ricinoleate, zinc oleate, ammonium laurate, zinc linoleate, ammonium myristate, triethanolamine naphthenates, zinc naphthenate, ammonium palmitate, zinc resinate, ammonium stearate, triethanolamine abiate, ammonium undecylenate, aluminum palmitate, aluminum stearate, aluminum oleate, barium stearate, and barium naphthenate.

[0050] (E) Olefins:
Linear C_{14} alpha-olefin, and linear C_{16} alpha-olefin.

[0051] (F) Phosphorous Compounds and Mercaptans:
POE octyl phosphate, sodium phosphated castor oil, ammonium phosphated castor oil, 2-ethylhexyl polyphosphate sodium salt, capryl polyphosphate sodium salt, sodium di(2-ethylhexyl)phosphate, lecithin (soy phospholipids), and POE (polyoxyethylene) tert-dodecylmercaptoethanol.

[0052] (G) Polyethylene and Propylene Glycol Esters:
Hydroxyethyl laurate, PEG monooleate, propylene glycol monolaurate, hydroxyethoxylaurate, PEG dioleate, ethylene glycol monoricinoleate, propylene glycol monostearate, hydroxy ethoxethoxy ethyl laurate, diethylene glycol monocinolionate, propylene glycol dilaurate, PEG monooleate, PEG monoricinolionate, propylene glycol distearate, PEG dilaurate, diethylene glycol cocoonate, ethylene glycol monostearate, dipropylene glycol monostearate, POE coco fatty acids ester, diethylene glycol monostearate, propylene glycol monooleate, POE castor oil, triethylene glycol monostearate, ethylene glycol hydroxyxystearate, propylene glycol monoricinolionate, PEG monooleate, PEG triglycride, stearate, propylene glycol monoisooleate, ethylene glycol distearate, POE hydroxylated castor oil, propylene glycol monohydroxystearate, PEG distearate, POE tall oil, PEG monoisooleate, POE abietic acid, propylene glycol dipalmitate, PEG disosteinate, POE linolein, hydroxyethyl oleate, acetylated lanolin, isopropylester of lanolin fatty acids, hydroxyethyleneyl olante, POE linolein acetylated, methoxy PEG monooleate, POE propylene glycol monostearate, and hydroxy ethoxethoxy ethyl oleate.

[0053] (H) Alcohols, Phenols and Polyoxyethylene Derivatives:
Stearyl alcohol, oleyl alcohol, octyl phenol, nonyl phenol, tert-octyphenoxie ethanol, p-dodecyl phenol, dinonyl phenol, tridecyl alcohol, tetradecyl alcohol, lanolin alcohols, cholesterol, dimethyl hexynol, dimethyl octynediol, tetramethyl decynediol, POE tridecyl phenyl ether, POE lanolin alcohol ether, POE cholesterol, POE n-octyphenol, POE tert-octylphenol, POE nonylphenol, POE dinonyl phenol, POE dodecyl phenol, POE lauryl alcohol ether, POE etyl alcohol ether, POE stearyl alcohol ether, POE tetrathyldecynediol, POE oleyl alcohol ether, POP (polyoxypropylene) EIO, POE isobutyl alcohol ether 2,6,8-trimethyl-4-nonyloxypropyleneoxyethanol, polyoxypropylene-polyoxyethylene block copolymer, alkyl ether of POE/POP, and POE tridecyl alcohol ether.

[0054] (I) Glycerol Esters:
Glycerol monoacrylate, glycerol monolaurate, glycerol mono/di/oleate, glycerol dilaurate, glycerol monostearate, glycerol monostearate distilled, glycerol distearate, glycerol monooleate, glycerol dioleate, glycerol trioleate, glycerol monoisooleate, glycerol monoricinoleate, glycerol monostearate, glycerol mono- undecylenate, POE glycerol monostearate, acetylated glycerol monooleate, succinylated glycerol monostearate, dicetylated glycerol monostearate tartrate, modified glycerol phthalate resin, triglycerol monostearate, triglycerol monooleate, triglycerol monoisooleate, decaglycerol tetraoleate, decaglycerol decaoleate, pentaerythritol monolaurate, pentaerythritol monooleate, pentaerythritol stearate, pentaerythritol tristearate, pentaerythritol monooleate, pentaerythritol oleate, pentaerythritol tristearate, pentaeryth-
ritol tetraricinoleate, sorbitan monolaurate, POE sorbitan monolaurate, sorbitan monopalmitate, POE sorbitan mono-
palmitate, sorbitan monostearate, POE sorbitan tristearate, POE sorbitan monooleate, sorbitan sesquioleate, sorbitan trioleate, POE sorbitan trioleate, POE sor-
tol hexaoleate, POE sorbitol olate laurate, POE sorbitol polyoleate, POE sorbitol, beeswax-ester, sorcose monola-
urate, sorcose cocoa, sorcose monomyristate, sorcose mono-
palmitate, sorcose dipalmitate, sorcose monostearate, sorcose distearate, sorcose monocteole, sorcose dioleate, laur-
yl lactate, cetyl lactate, sodium lauryl lactate, sodium stearoyl lactate, sodium isostearoyl-2-lactylate, sodium stea-
royl-2-lactylate, calcium stearyloyl-2-lactylate, sodium capryl lactate, lauryl alcohol, and cetyl alcohol.

[0055] (J) Amides and Amide Derivatives:
Stearamide, oleamide, erucamide, behenamide, lauric acid monooctanamide, lauric acid monostearamide, POE lauric amide, myristic acid diethanolamide, stearic acid diethanol-
amide, oleic acid diethanolamide, POE oleic amide, coco acid diethanolamide, POE coco amide, POE hydrogenated tallow amide, lauric acid monoisopropanalalamide, and oleic acid monoisopropanolamidem.

[0056] (K) Sulfates:
Sodium n-octyl sulfate, sodium 2-ethylhexyl sulfate, sodium dectyl sulfate, sodium lauryl sulfate, sodium trietyl sulfate, sodium sec-tetradecyl sulfate, sodium cetyl sulfate, sodium sec-octadecyl sulfate, sodium oleyl sulfate, sodium oleyl stea-
rinate, sodium triethyl ether sulfate, potassium lauryl sulfate, magnesium lauryl sulfate, triethanolamine lauryl sulfate, ammonium lauryl sulfate, diethanolamine lauryl sul-
fate, triethanolammonium lauryl sulfate, POE octylphenol sodium salt, alkylaryl polyether sulfate sodium salt, sulfated POE nonylphenol sodium salt, sulfated nonylphenyl ether of tetraethyleneglycol ammonium salt, sulfated lauryl ether of tetraethyleneglycol sodium salt, POE sodium lauryl mono-
ether sulfate, POE sodium lauryl ether sulfate, POE ammonium lauryl sulfate, sulfated oleic acid sodium salt, sulfated castor oil-fatty acids sodium salt, sulfated propylene glycol sodium salt, sulfated isopropylglycol sodium salt, sulfated butylglycol sodium salt, sulfated glyceral monolaurate sodium salt, sul-
fated glycerol tristearate sodium salt, sulfated castoroil sodium salt, sulfated oleylamine sodium salt, sulfated neotroil sodium salt, sulfated rice bean oil sodium salt, sulfated soya bean oil sodium salt, sulfated synthetic sperm oil, and sulfated tallow sodium salt.

[0057] (L) Miscellaneous Surfactant Compounds:
Perfluro surfactant-anionic, perfluro surfactant-cationic, ethylhexadiminetetraacetic acid disodium salt, ethylhexeded-
aminetetraacetic acid tetradsodium salt, sodium dihydroxyethyl glycinate, trisodium nitritolactacetate, sodium citrate, sil
cone defoamer-oil, silicone defoamer-water dispersible, sodium tetraborate, sodium carbonate, sodium phosphates-
tribasic, sodium silicate, and alkyl benzene sulfonic acid-propylene tetramer.

[0058] (M) Sulfonates:
Sodium tolue sulfinolate, sodium xylene sulfinolate, sodium cumene sulfinolate, sodium dodecylbenzene sulfinolate, sodium triethylbenzene sulfonate, sodium kerylbenzene sul-
fonate, calcium dodecylbenzene sulfinolate, ammonium xylene sulfinolate, triethanolamminium dodecylbenzene sul-
fonate, alkylammonium dodecyl-benzene sulfinolate, alipha
tic hydrocarbons-sulfonic acid, sodium petroleum sul-
fonate, calcium petroleum sulfinolate, Bryton barium sul-
fonate, magnesium petroleum sulfonate, ammonium petroleum sulfinolate, isopropylamine petroleum sulfinolate, ethylenediamine petroleum sulfinolate, triethanolamine petroleum sulfinolate, sulfonated naphthalene sodium diisopropyl naphthalene sulfinolate, sodium dibutyl napththalene sulfinolate, sodium benzyl napthalene sulfinolate, sodium naphthalene formaldehyde-condensate sulfinolate, sodium polymerized alkylnaphthalene sulfinolate, potassium polymerized alkyl-
naphthalene sulfinolate, ammonium dibutyl naphthalene sul-
finolate, ethanolamine dibutyl naphthalene sulfinolate, sodium sulfoleate, sodium monobutylphenylphenol monosulfonolate, disodium dibutylphenylphenol disulfonate, potassium mono-
ethylphenylphenol monosulfonate, ammonium monooctyl-
phenylphenol monosulfonate, guanidinium monooctylphen-
phenol sulphonates, sodium decylidiphenylether disulfonate, sodium dodecylidiphenylether disulfonate, cal-
cium polymerized alkyl-benzene sulfinolate, sulfonated poly-
syrene, sulfonated aliphatic polyester, sodium-2-sulfoethyl oleate, sodium anyl sulfooleate, sodium lauryl sulfoacetate, sodium diisobutyl sulfoacacetate, sodium diamin sulfoacacetate, sodium dibexyl sulfoacacetate, sodium diotyl sulfoacacetate, sodium ditridecyl sulfoacacetate, sodium alkylarylpolyether sulfinolate, and sodium lignosulfonate.

[0059] (N) Amines and Amine Derivatives:
tert-C_{14}-C_{16} amine, n-dodecylamine, n-tetradecylamine, n-hexadecylamine, n-octadecylamine, C_{16}-C_{24} amine, oley-
lamine, cocomine, hydrogenated tallow amine, tallow amine, POE ten-amine, POE stearyl amine, POE oleyl amine, C_{12}-C_{14} tert-alkylamines, ethoxylated POE cocomaine, POE tallow amine, POE soya amine, POE octadeylamine, N-b-
hydroxyethyl stearyl imidazoline, POE (3) N-tallow trimethylene diamine, N-b-hydroxyethyl cocoimidazoline, N-b-hy-
droxyethyl oleyl imidazoline, N-dodecylamine acete, hexadecylamine acetate, octadecyiylene acetate oleylamine acetate, cocomine acetate, hydrogenated tallow amine acetate, tallow amine acetate, soya amine acetate, N-stearyl-N'-N'-diethylethylene-diamine acetate, N-oleylethylendia-
mine formate, cocomidopropyl dimethyl amine oxide, lau-
ryl dimethylamine oxide, myristyl dimethylamine oxide, so-
ya amine, diococamine, dihydrogenated tallow amine, di-
methyl hexadecyamine, dimethyl octadeylamine, dim-
ethyl cocoamine, dimethyl soyaamamine, N-coco-1,3-diamino-
propane, N-soya-1,3-diaminopropane, N-tallow-1,3-diamino-
propane, N-coco-b-aminobutyric acid, stearamidoethyle-
diethyline, sodium-N-coco-b-amine propionate, N-tallow trimethylene diamine diacetate, disodium-N-tallow-b-imino dipropionate, disodium-N-lauryl-b-imino dipropionate, cetyl betaine, cocoo betaine, myristamidopropyl betaine, oleyl betaine, coconut amido betaine, oleyl amido betaine, coconut oil acid ester of sodium isethionate, cocomaido alkyltrimethyl-
amine, behenic amido alkyl dimethylamine, isostearic amido alkyl
dimethylamine, oleic amido alkyl dimethylamine, sodium-N-methyl-N-palmitoyl taurate, sodium-N-methyl-
N-oleyl taurate, sodium-N-coconut acid N-methyl taurate, sodium-N-methyl-N-tall oil taurate, N-lauryl sarcosine, cocoy sarcosine, N-oleyl sarcosine, sodium-N-lauryl saro-
cinate, sodium carboxymethylglycidolhydroxy-ethyl imidazo-
linium hydroxide, sodium carboxymethylglycidolhydroxy-ethyl imidazolium hydroxide, sodium carboxymethylglycidolhydroxy-ethyl imidazolium hydroxide, sodium carboxymethylglycidolhydroxy-ethyl imidazolium hydroxide, sodium carboxymethylglycidolhydroxy-ethyl imidazolium hydroxide, and sodium carboxymethylsodium-
carboxy-ethyl cocoether imidazolium.
(0) Quaternary Amine Salts:
Dodecyltrimethyl ammonium chloride, hexadecyltrimethyl ammonium chloride, octadecyltrimethyl ammonium chloride, cetyltrimethyl ammonium bromide, cetyltrimethyl ammonium chloride, cocooctyltrimethyl ammonium chloride, and cetyltrimethyl ammonium chloride. Other useful emulsifiers include sorbitan monolaurate (Span® 80) and sorbitan monopalmitate (Span® 40) available from Sigma Aldrich, polyethyleneol(20)sorbitan trioleate (Twee), polyethyleneol(20)sorbitan monopalmitate (Twee 40) and polyethyleneol(20)sorbitan monolaurate (Twee 20).

Useful emulsifiers can include compounds exhibiting a hydrophilic-lipophilic balance (HLB), which refers to the size and strength of the polar (hydrophilic) and non-polar (lipophilic) groups that comprise the emulsifier or surfactant molecule) typically in the range of 1 to 24; in another embodiment about 1 to 20. HLB is a well-known parameter utilized by those skilled in the art for characterizing emulsifiers. In some embodiments, the emulsifier has an HLB in the range of about 1 to 20; in one embodiment about 1 to 20; and in another embodiment about 4 to 18; alternadively, greater than about 8, for example about 8.5 or about 9 to about 18. Various useful compounds include those identified herein, including for example, sorbitan monolaurate, polyethyleneol(20) sorbitan monoleate, and polyethyleneol(20) sorbitan monopalmitate.

It is also possible to obtain stable emulsified fuel compositions using a combination of emulsifiers. For purposes of explanation and not limitation, for example instead of a single emulsifier having an HLB value of about 12, an emulsified fuel composition can be prepared using a mixture of emulsifiers, such as a 50/50 mixture two emulsifiers, one having an HLB value of about 16 and the other an HLB value of about 8. Similarly combinations of three or more emulsifiers can also be used, provided that the HLB value of the mixture exhibits the desired overall value and the effect of the mixture is to provide a stable emulsion. For purposes of a mixed emulsifier composition, the HLB value of the emulsifier mixture is calculated as a linear sum weighted average based on the weight fraction that each of the emulsifiers represents compared to the total amount of emulsifier present. In some embodiments, a mixture of two emulsifiers is used wherein one emulsifier has an HLB value of equal to or less than about 0.5, such as about 1 wt% to about 5 wt%, or about 1 wt% to about 4 wt%, or about 1 wt% to about 3 wt%, or about 3 wt% to about 2 wt%. Alternatively, the concentrations of various hydrophilic or substantially hydrophilic emulsifiers can be added together for consideration of the above recited concentrations, including water, hydroxyl-containing compound(s) such as one or more alcohols or glycols and the like. In particular, if the ratio of the total amount of such hydrophilic components to the total amount of lipophilic components, the latter including but not limited to the pyrolysis oil, is equal to or less than about 0.5, for example, about 0.05 to about 0.25 or any specific value there between, including, for example, about 0.06, 0.08, 0.10, 0.12, 0.14, 0.16, 0.18, 0.20, 0.22 or 0.24, it may be desirable to use a mixture of emulsifiers as described above; in other words, emulsifier mixtures wherein at least one emulsifier has an HLB value of equal to or less than about 6 and at least one emulsifier has an HLB value of greater than about 6 (subject to the provisos expressed above). In some embodiments, to prepare a stable emulsion using such components, a mixture of emulsifiers may be employed, for example, a 50/50 mixture of an emulsifier having an HLB value of, for example, about 4 and one having an HLB value of about 15. In contrast, a stable emulsified composition can be prepared using a single emulsifier where the lipophilic and hydrophilic components comprise about 75 wt% pyrolysis oil, 1 wt% water, and 25 wt% alcohol. Alternatively, a mixture of emulsifiers can be used even where the calculated ratio is greater than 0.25, particularly if the value is only slightly greater, for example about 5% to about 10% greater. Optionally, a mixture of emulsifiers can be used if desired; particularly if it is anticipated that the user of such a fuel composition may subsequently introduce an additive into the composition that might have the effect of changing the calculated ratio.

Alcohols

Embodiments of the invention may include one or more alcohols which, among other things, increase the pH to
improve the acidity of the pyrolysis oil fuel, reduce the final viscosity, and enhance the ignition properties of the final fuel. Alcohols useful in the present invention include hydroxyl-containing organic compounds selected from the group consisting of (A) monohydric (one OH group) alcohols characterized as (1) aliphatic, including straight and branched chain, and sub-characterized within this group as paraffinic (for example, ethanol) and olefinic (for example, allyl alcohol); (2) alicyclic (for example, cyclohexanol); (3) aromatic (for example, phenol, benzyl alcohol); (4) heterocyclic (for example, furfuryl alcohol); and (5) polycyclic (for example, sterols); (B) dihydric (two OH groups), including glycols and derivatives (for example, diols); (C) trihydric (three OH groups), including glycerol and derivatives; and (D) polyhydric (polysols), having three or four or more OH groups. In particular, useful alcohols include alcohols selected from the group consisting of C1 to C4 straight and branched chain monoalcohols, C2 to C4 mono- and polyalkylene glycols including ethylene glycol, diethylene glycol, triethylene glycol, propylene glycol, dipropylene glycol, tripropylene glycol, derivatives of C2 to C4 mono- and polyalkylene glycols provided that the molecular weights of such polyalkylene glycols are suitable for use in the fuel compositions of the present invention, and mixtures thereof. In some embodiments, fuel compositions in which a monoalcohol is included may also include at least one of tert-butyl alcohol, at least one C2-C4 alkyglycol or a mixture of both. In some embodiments, ethyl alcohol or ethanol and propylene glycol may be preferred. Ethanol is available commercially in the anhydrous form (also referred to as absolute alcohol or 100% ethanol) and as various proofs or percentages of ethanol where the additional component in the ethanol is water, the most common being 190 proof or 95 vol %. If ethanol is used for purposes other than as a beverage, it is denatured by addition of substances, such as methanol, 2-propanol, ethyl acetate, methyl isobutyl ketone, heptane or kerosene, to make the product undesirable for human consumption, but allows for its use for industrial purposes, including as a component in fuel or as a fuel. As noted, ethanol other than absolute ethanol is typically identified by use of the term “proof,” where the conversion between proof and the concentration of ethyl alcohol is that 2 proof equals 1% by volume, typically measured at 20°C, although measurements at other temperatures are also accepted, including e.g., 15.6°C. While various denaturants are available that can render ethanol (with or without the presence of moisture or water) unsuitable for human consumption, certain of such denaturants may not be suitable for use in connection with fuels because of their adverse effects on fuel stability, vehicle engines and fuel systems and emissions. A list of denaturants used in connection with ethyl alcohol for various purposes can be found in The Merck Index, Thirteenth Edition, 2001, entry 3796, page 670. When used in the pyrolysis oil emulsion fuel composition of the present invention, alcohol or a mixture of the alcohols identified herein as useful, are included at a concentration of about 0 wt % to about 30 wt % based on the total weight of the fuel composition; or about 1 wt % to about 30 wt %; or about 2 wt % to about 20 wt %; or about 5 wt % to about 10 wt %; or about 7 wt % to about 8 wt %.

Alternatively, the C4 alcohol butyl alcohol is also useful in the present invention. Where butyl alcohol is used it may be the tert-butyl alcohol because it is more readily soluble in water. However, n-butyl alcohol and sec-butyl alcohol are not completely soluble in water, they may be used with adjustment in the type and amount of emulsifier in the fuel composition in order to obtain a stable emulsion. Tert-butyl alcohol can be used in place of or in combination with ethanol, for example including mixtures in which the relative amount, by weight, of ethanol to tert-butyl alcohol is about 95/5 to 5/95; including useful amounts therebetween such as about 85/15, 80/20, 75/25, 70/30, 65/35, 60/40, 55/45, 50/50, 45/55, 40/60, 35/65, 30/70, 25/75, 20/80, 15/85, and about 10/90.

Additives

Optionally, additives may be added to the emulsifier, the pyrolysis oil, the water or combinations thereof. The additives include but are not limited to cetane improvers, organic solvents, other fuels such as diesel fuel, glycols, surfactants or emulsifiers, other additives known for their use in fuel and the like. The additives are added to the emulsifier, pyrolysis oil or the water prior to, or in the alternative at, the emulsification device(s), depending upon the solubility or other fluid properties of the additive. The additives are generally in the range of about 1% to about 40% by weight, in another embodiment about 5% to about 30% by weight, and in another embodiment about 7% to about 25% by weight of the fuel mixture.

An optional component that may be used as an additive to the fuel mixture is supplementary combustible liquid such as “paint thinner,” turpentine or mineral spirits. The supplementary combustible may be characterized as a low viscosity, low density supplementary combustible liquid additive. Such an optional component can be useful for the purpose of modifying one or more properties of the fuel composition, including, for example, the cetane number, density and viscosity. Consequently, the amount and type of such component can be selected based on its combustion properties as measured by the cetane number of the resulting fuel composition, by the density of the resulting composition and by its viscosity as well as its effect on the phase distribution of the microemulsion in view of the amount and type of surfactant used. In each instance the amount of the liquid added can be suitably adjusted to produce a fuel composition having the overall balance of properties suitable for the end use of the fuel product, for example, as a fuel for a diesel engine, a furnace, etc., or for adjusting the properties of the fuel composition for the ambient temperature environment in which it is intended to be used, for example, as an automotive diesel fuel for winter or summer use.

Useful supplementary combustible liquid additives of the paint thinner type include products identified as hydrotreated, light steam cracked naphtha residuum (petroleum), also referred to as naphtha, petroleum, hydrotreated heavy, and identified as CAS 64742-48-9. This product has also been described as a complex combination of hydrocarbons obtained by treating a petroleum fraction with hydrogen in the presence of a catalyst.

Supplementary combustible liquids useful in the present invention can include a broad range of petroleum distillate materials as well as supplementary combustible liquids from other sources, for example, plant or vegetable sources. Useful products generally boil in the range of about 145°C to about 200°C. Turpentine is a supplementary combustible fluid that could be used.

Turpentine substitute is a mineral oil based replacement for the vegetable-based organic solvent turpentine and it is suitable for use herein. It is a hydrotreated light distillate of
petroleum, which forms a clear transparent liquid at ambient or room temperature. It is a complex mixture of highly refined hydrocarbon distillates mainly in the C9-C16 range. The liquid is highly volatile and the vapors are flammable. It is a widely available as a less costly substitute for turpentine. It is commonly used as an organic solvent in painting and decorating, for thinning oil based paint and cleaning brushes. Also known as turps substitute, mineral turpentine, or simply turps, which can cause confusion with vegetable-based turpentine.

[0073] White spirit, also known as Stoddard solvent is also suitable for use herein. It is a paraffin-derived clear, transparent liquid which is a common organic solvent used in painting and decorating. It is a mixture of saturated aliphatic and alicyclic C7 to C12 hydrocarbons with a maximum content of 25% of C7 to C12 alkyl aromatic hydrocarbons. White spirit typically is used as an extraction solvent, as a cleaning solvent, as a degreasing solvent and as a solvent in aerosols, paints, wood preservatives, lacquers, varnishes, and asphalt products. In western Europe about 60% of the total white spirit consumption is used in paints, lacquers and varnishes. White spirit is the most widely used solvent in the paint industry.

[0074] The various fluids identified as “mineral spirits” are suitable for use as a supplementary combustible fluid in the present invention. Mineral spirits is commonly used as a paint thinner and mild solvent and is suitable for use herein. In Europe, it is referred to as petroleum spirit. They are especially effective in removing oils, greases, carbon and other material from metal. Mineral spirits is derived from the light distillate fractions during crude oil refining and comprise C6 to C11 compounds, with the majority being C9 to C11. There are many different substances generally referred to as mineral spirits and each generally has a different CAS number. One common type is mineral oil spirits identified as CAS 64475-85-0, Stoddard solvent, referred to above is a particular type, subcategory or subset of mineral spirits, identified as CAS 8052-41-3 and contains 30-62 wt % alkanes, 27-40 wt % cycloalkanes, 0.3-20 wt % alkylbenzenes, 0.007-0.1 wt % other benzenes, 0.2 wt % naphthalenes and 0.3 wt % acenaphthenes. Commercial Stoddard Solvent products are available under the trade names Varanol 1 and Texosolve S. Similarly, benzine is another, subset of mineral spirits comprising C5 to C9 hydrocarbons and boiling at about 154°C to about 204°C. Mineral spirits on the other hand comprise 20-65 wt % alkanes, 15-40 wt % cycloalkanes and 10-30 wt % aromatics; the specific amount of each varying depending on the particular “mineral spirit” being considered.

[0075] Another supplementary combustible liquid that can be used is kerosene. Kerosene is typically defined as a refined petroleum solvent (predominantly C8-C16 hydrocarbon, which is typically a mixture of 25% normal paraffins, 11% branched paraffins, 30% monocycloparaffins, 12% dicycloparaffins, 1% tri cycloparaffins, 16% mononuclear aromatics and 5% dinuclear aromatics. Alternatively, a product known as hydrotreated kerosene (CAS No. 64742-47-8) can be used. As its name suggests, it is derived from kerosene, or straight run kerosene, by hydrogenation in order to saturate the double bonds present in various molecules of kerosene.

[0076] Various chemical compounds have been identified that have the ability to improve the cetane number of diesel fuel. Where necessary or desired to meet specific performance requirements in certain applications, one embodiment of the pyrolysis oil-based water-fuel emulsion compositions of the present invention can optionally include one or more compounds having the ability to increase cetane number.

[0077] One useful type of cetane improver is nitrated alcohol esters such as tetraethyl glycol nitrate. Cetane improvers can be added to tailor the final cetane number of the pyrolysis oil fuel. Other useful cetane improvers include but are not limited to one or more of peroxides, nitrates, nitrites, nitrocarbamates, mixtures thereof and the like. Useful cetane improvers include but are not limited to nitropropane, nitropentane, tetranitromethane, 2-nitro-2-methyl-1-butan, 1-methyl-2-nitro-1-propanol, and the like. Also included are nitrate esters of substituted or unsubstituted aliphatic or cyclic aliphatic alcohols which may be monohydrate or polyhydrated. These compounds include substituted and unsubstituted alkyl or cycloalkyl nitrates having up to about 10 carbon atoms, and in one embodiment about 2 to about 10 carbon atoms. The alkyl group may be either linear or branched, or a mixture of linear or branched alkyl groups. Examples of such 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, n-heptyl nitrate, n-octyl nitrate, 2-ethylhexyl nitrate, sec-octyl nitrate, n-nonyl nitrate, n-decyl nitrate, cyclopentyl nitrate, cyclohexyl nitrate, methylcyclohexyl nitrate, and isopropylcyclohexyl nitrate. Also useful are the nitrate esters of alkoxy-substituted aliphatic alcohols such as 2-ethoxyethyl nitrate, 2-(ethoxy-ethoxy)ethyl nitrate, 1-methoxypropyl-2-nitrate, 4-ethoxybutyl nitrate, etc., as well as dial nitrates such as 1,6-hexamethylenediamine. A useful cetane improver is 2-ethylhexyl nitrate.

[0078] Organic peroxides can also be useful as cetane improvers in the fuel compositions herein. Generally useful compounds are dialkyl peroxides of the formula R1OR2 wherein R1 and R2 are the same or different alkyl groups having 1 to about 10 carbon atoms. Suitable peroxide cetane improver compounds should be soluble in the fuel composition and thermally stable at typical fuel temperatures of operating engines. Peroxides wherein R1 and R2 are tertiary alkyl groups having 4 or about 5 carbon atoms are especially useful. Examples of suitable peroxides include di-tertiary butyl peroxide, di-tertiary amyl peroxide, diethyl peroxide, di-n-propyl peroxide, di-n-butyl peroxide, methyl ethyl peroxide, methyl t-butyl peroxide, ethyl t-butyl peroxide, propyl t-amyl peroxide, mixtures thereof and the like. In some embodiments, peroxides may exhibit one or more of the following characteristics: good solubility in the fuel, suitable water partition coefficient characteristics, good thermal stability and handling characteristics, have no impact on fuel quality or fuel system components, and have low toxicity. A useful peroxide is di-tertiary butyl peroxide, also sometimes referred to as tertiary butyl peroxide.

[0079] Other suitable optional ingredients can be included in the compositions of the present invention provided that they do not substantially adversely affect performance of the composition and its intended use. Included in the category of such other optional ingredients would be, for example, thermal and aging stabilizers; coloring agents, dyes and markers, particularly those permitted in the European Union as set forth in EN 14214:2003-5.1; agents to modify the odor of the mixture in order to prevent inadvertent ingestion, including, for example, aldehydes; etc. Alternatively, and if necessary, agents can be added in a suitable amount, typically at a low concentration, that are capable of modifying or masking an
unpleasant odor or smell, if any, of the exhausted gas after combustion. Other conventional additives and blending agents for fuel compositions of the present invention may be present. For example, the fuels of this invention may contain conventional quantities of such conventional additives as rust inhibitors such as alkylated succinic acids and anhydrides, inhibitors of gum formation, metal deactivators, upper cylinder lubricants, friction modifiers, detergents, antioxidants, heat stabilizers, bacteriostatic agents, microbicides, fungicides and the like. Such conventional additives may be present in the fuel composition at concentrations of up to about 1 wt% based on the total weight of the water-pyrolysis oil fuel emulsion; for example about 0.01 wt% to about 1 wt%.

The amount of additives used can be suitably varied, depending upon the purpose for which the additive is used and the use of the final fuel product, for example. In some embodiments, the additive may be used at about 0.1 wt% to about 30 wt%. In other embodiments, the additive may be present at about 1 wt% to about 25 wt%. In embodiments for use with engines, the additive may be present at about 10 wt% to about 30 wt%, for example. In embodiments for use with burners and heaters, the additives may be present at about 10 wt% to about 20 wt%, for example. In some embodiments, higher amounts of additives can be used, for example, about 35 wt% or about 40 wt% or up to about 45 wt%.

Emulsification

The water-pyrolysis oil fuel emulsions comprise a pyrolysis oil fuel phase and a water or aqueous phase. Either the pyrolysis oil fuel phase or the aqueous phase may comprise the continuous phase, with the other phase comprising the discontinuous or dispersed phase, depending upon the method of preparation of the fuel. The dispersed phase, being either the pyrolysis fuel phase or the aqueous phase, may be comprised of droplets having a mean diameter of about 25 microns or less, for example, 5 microns.

The emulsions may be prepared by various steps or sequences of addition as described. For example, the steps may include (1) mixing the pyrolysis oil and one or more emulsifiers and other optional desired additives using standard mixing techniques to form a pyrolysis oil-emulsifier mixture; (2) separately mixing water and alcohol and other optional desired additives; and (3) mixing the pyrolysis oil-emulsifier mixture with the water/alcohol mixture under emulsifying mixing conditions to form the desired water-pyrolysis oil fuel emulsion. Additional optional additives may be added, such as during step 3, including for example ethanol, propylene glycol, cetane improver, or mixtures thereof.

The water/alcohol mixture can optionally include, but is not limited to, one or more alkylation glycol, alcohol, cetane improver or mixtures thereof. In one embodiment the water, alcohol and/or alkylation glycol and/or the cetane improver are mixed with one another and fed continuously to the pyrolysis oil/surfactant mixture. In another embodiment the water, alcohol and/or alkylation glycol and/or the cetane improver or mixtures thereof flow out of separate tanks, or various combinations thereof flow out of separate tanks, into the emulsification device. In one embodiment the water, alcohol and/or alkylation glycol and/or the cetane improver or mixtures thereof meet the pyrolysis oil fuel additives mixture immediately prior to or in the emulsification device.

An exemplary flow chart showing the production of 1,000 kilograms of pyrolysis oil based biofuel is shown in FIG. 1. In step (a), pyrolysis oil (728 kg) is offloaded into a main mix tank (MMT). While offloading the pyrolysis oil, the mechanical mixer and forwarding pump are turned on and optionally 1.0 kg of the ultra low sulfur diesel (ULSD) fuel is added to the main mix tank in step (b). In step (c), while mixing with the mechanical mixer, 8.5 kg of Hypermer® 1083 is added to the main mixer. In step (d), while mixing with the mechanical mixer, 2.5 kg of Incombustible CDEA is added. After all additions are made, the level of the tank is recorded. The mixture is processed until the contents are well mixed, for at least one turn of the tank contents. After the tank contents are well mixed, the valving is opened and mixing of the contents of the tank is continued, then the mixers are turned off and the valves are closed.

The maximum amount of material, including water and alcohols, to be put into the secondary mix tank is calculated according to the size of the secondary mix tank. This is the so called hydration phase, in which a first batch, such as 30% of the water and ethylene glycol mixture, will be separately prepared and added to the main mix tank and mixed for a period of time. The water and ethylene glycol mixture can be separately prepared and added in multiple batches, such as 2, 3, 4 or 5 batches, or can be prepared all at once and added in discrete batches. This will define the number of times the secondary mix tank will need to be filled.

The secondary mix tank is filled with 57 kg, water (30% of 190 kg) in step (f) as the amount required for the hydration phase. In step (g), the secondary mix tank is filled with 21 kg ethylene glycol (30% of 70 kg) as the amount required for the hydration phase. The water/glycol solution is mixed for at least 10 minutes. While mixing with the mechanical mixer, the glycol solution from the secondary mix tank is transferred to the main mix tank in step (h). The mixers are turned on and the valves of the main mix tank are opened to allow flow of the tank mixture. The mixture is processed until the contents are well mixed, for at least one turn of the tank contents, in step (i).

In step (j), the secondary mix tank is filled with the second amount of water, 133 kg. (which is 190 kg - 57 kg). In step (k), the secondary mix tank is filled with the second amount of ethylene glycol, 49 kg (which is 70 kg - 21 kg). The water and glycol solution are mixed for at least 10 minutes.

While mixing the main mix tanks with the distributors, perforated line, and mechanical mixer, the water/glycol solution is slowly transferred to the main mix tank in step 1. The mixers are turned on and the valves are opened to allow flow of the tank mixture. The mixture is processed until a stable emulsion has been achieved.

Once a stable emulsion has been achieved, the mechanical mixer can be shut off with valves closed and the contents of the main mix tank can be routed to a transport tank or product storage as a finished product in step m.

Various mixing devices well known in the art can be employed to facilitate formation of an emulsified composition including, for example, mixer-emulsifiers, which typically utilize a high speed rotor operating in close proximity to a stator (such as a type made by Charles Ross & Sons Co., NY), paddle mixers utilizing paddles having various design configurations including, for example, reverse pitch, anchor, leaf, gate, finger, double-motion, helix, etc., including batch and in-line equipment, and the like. Other methods of mixing useful in this embodiment as well as generally in the present
invention are further described herein below. The processes of various embodiments of the present invention can be carried out at a convenient temperature, including, for example, at ambient or room temperature, such as about 20°C to about 22°C or even as low as about 5°C and as high as about 32°C. The time and temperature of mixing can be varied provided that the desired emulsified composition is achieved and, based on subsequent observation and/or testing, it is suitably stable until it is used, as well as during use. Under conditions wherein sediment may form following mixing of the components of the fuel composition, it can be desirable to wait for a period of time in order to allow for sedimentation, if any, to occur, such material to subsequently be removed or separated from the emulsified fuel composition. Typically, such time period is at least about 4 minutes; in some embodiments, it is about 5 minutes; in still other embodiments, it is about 6 minutes or more. The amount of time can readily be determined with limited and simple experiments and such time can be adjusted, based on, for example, the type, quality and composition of the pyrolysis employed, as well as the other components of the mixture, including emulsifier(s).

[0091] Mixing methods in addition to those described above may be suitable for use in some embodiments. Mixtures can be prepared with traditional mixing or blending equipment such as vats or tank equipped with motor driven stirrers having various configurations, e.g., paddle, helix, etc. Mixing carried out in such equipment may be time consuming, in some cases requiring greater than 10 minutes of mixing, for example about 10 to about 30 minutes, alternately about 15 to about 20 minutes, in order to achieve a uniform and stable emulsion. However, such emulsions contain dispersed particles having an average particle size, e.g., diameter or average dimension on the order of greater than about 20 microns; for example about 20 to about 50 microns; alternatively about 20 to about 35 microns. Emulsions having an average particle size of about 20 microns or greater are referred to as macroemulsions. A fuel composition having macroemulsion characteristics will typically exhibit properties that differ from the same fuel composition having an average particle size that is significantly smaller, in other words, a microemulsion or one in which the particle size is less than about 20 microns, such as 19 microns or less. For example, a given composition in macroemulsion form may exhibit a higher viscosity, lower flash point and poorer stability in a process requiring extended recirculation of the fuel composition as well as requiring a greater amount of emulsifier in order to produce a satisfactory and stable emulsion compared to the same composition in microemulsion form.

[0092] In one method, fuel mixtures of the present invention are prepared using ultrasonic mixing equipment, which equipment may produce stable emulsions having a small particle size, for example less than about 10 microns, or about 0.01 to about 5 microns on average, in other words embodiments of a microemulsion. Equipment of this type is available commercially as Sonolator ultrasonic homogenizing system, available from Sonic Corp., of Stratford, Conn. Such microemulsions may be prepared at ambient temperature, for example about 22°C, and at pressures of about 500 psi to about 1500 psi, although pressures as high as 5000 psi can also be used to produce stable microemulsions. The Sonolator system may be useful in that it can be operated in alternative, useful modes, including semi-continuous, continuous, single-feed or multiple-feed. In particular, such a system operated in multiple-feed mode can utilize feed tanks containing, for example, pyrolysis, water, emulsifier and other components, such as alcohol, cetane enhancer, alkyl glycol or alkyl glycol derivative, etc. Such a system allows feeding of one or more of the components simultaneously, sequentially or intermittently in order to achieve a particularly desirable result, including but not limited to a specific emulsion particle size, particle size distribution, mixing time, etc. As noted above, fuel compositions prepared using ultrasonic emulsification can be accomplished using a lower concentration of emulsifier for the same concentration of other components, particularly the pyrolysis oil and water. For example, where a composition prepared without ultrasonic may require about 1.0 wt % emulsifier to obtain a satisfactory emulsion, it may only require less than about 0.5 wt % emulsifier with the same composition using an ultrasonic mixing equipment in order to obtain a satisfactory emulsion, such as an enhanced emulsion having a particle size that is smaller, resulting in a microemulsion. The amount of emulsifier may be about 10% less than would be required in the absence of ultrasonic emulsification; such as about 20% less; about 30% less; about 40% less. In some embodiments, about 50%, 60%, 70%, 80% or even 90% less of emulsifier may be required for a satisfactory emulsion with the use of ultrasonic energy input. For example, an emulsified fuel composition requiring 1 wt % emulsifier to obtain an average emulsion particle size of about 20 microns may be replaced with 0.2 wt % of the same emulsifier in the same composition to obtain an emulsion having a particle size of about 5 microns. For purposes herein, the use of a device that introduces ultrasonic energy for mixing and emulsification is referred to as a "high shear" method, regardless of the physical processes that may occur on a microscopic or molecular scale.

[0093] Emulsification using high shear such as imparted by an ultrasonic device results in an emulsion having a mean particle or droplet size in the range of about 0.01 microns to less than about 20 microns; such as about 0.01 microns to about 15 microns; or about 0.1 microns to about 10 microns; about 0.1 microns to about 8 microns; about 0.2 microns to about 6 microns; about 0.5 microns to about 5 microns; about 0.5 microns to about 4 microns; about 0.5 microns to about 3 microns; about 0.5 microns to about 2 microns; about 0.1 microns to about 1 microns or about 0.1 microns to about 1 micron or less, for example about 0.8 microns. According to one embodiment of the invention, the dispersed phase of the fuel composition comprises droplets having a mean diameter, or major dimension, of 5 microns or less.

[0094] High-shear devices that may be used include but are not limited to the Sonic Corporation Sonolator Homogenizing System, in which pressure can be varied over a wide range, for example about 500 to about 5,000 psi; IKA Work Dispa, and shear mixers including multistage, for example three stage rotor/stator combinations. The tip speed of the rotor/stator generators may be varied by a variable frequency drive that controls the motor. Silverson mixer two-stage mixer, which also incorporates a rotor/stator design and the mixer employs high-volume pumping characteristics similar to a centrifugal pump. Inline shear mixers employing a rotor/stator emulsification approach (Silverson Corporation); Jet Mixers, venturi-style/cavitation shear mixers; Microfluidizer shear mixers, high-pressure homogenization shear mixers (Microfluidics Inc.); and any other available high-shear generating mixer capable of producing the desired microemulsion, including high shear mixers selected from the group
consisting of Aquashear mixers (Flow Process Technologies Inc.), pipeline static mixers, hydraulic shear devices, rotational shear mixers, ultrasonic mixing, and combinations thereof.

[0095] Mixing of the components may be conducted at ambient, or substantially ambient, temperature conditions. It has been observed that in some instances mixing to obtain the emulsified fuel composition is accompanied by a slight exothermic response. Mixing can be satisfactorily conducted at temperatures in the range of about 5°C to about 75°C; for example about 10°C to about 65°C; or about 15°C to about 55°C; or about 20°C to about 45°C; such as 22°C to about 35°C.

EXAMPLES

[0096] For the following experiments, the components were combined using a lab mixer IKA RW20 digital. Low/medium mixing speed was in the range 700 to 1,100 rpm. Medium/high mixing speed was in the range 1,000 to 1,800 rpm.

Example 1

[0097]

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis oil</td>
<td>72.90</td>
</tr>
<tr>
<td>Water</td>
<td>19.00</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>7.00</td>
</tr>
<tr>
<td>Hypermel 1083SF</td>
<td>0.85</td>
</tr>
<tr>
<td>MONAMINE™ ADD-100</td>
<td>0.25</td>
</tr>
<tr>
<td>(Indromide™ CDEA)</td>
<td></td>
</tr>
</tbody>
</table>

A fuel mixture was prepared according to Table 1, including the following components: 729 grams pyrolysis oil; 190 grams water; 70 grams ethylene glycol; 8.5 grams of Hypermel 1083SF; and 2.5 grams MONAMINE™ ADD-100. The crude pyrolysis oil used in the example was produced from post consumer plastic treatment.

[0099] In one beaker, the non-ionic polymeric surfactant CORODA Hypermel 1083SF (0.85%) was added to the CORODA co-surfactant (0.25%) Monamine ADD-100. They were mixed using low-medium speed/shear for a few minutes (about 4 minutes). (Alternatively, they could be mixed for from about 1-20 minutes, depending upon the quantity of fuel being produced.) The blend of the two surfactants was added to the crude pyrolysis oil feedstock (72.90%) and mixed at medium/high speed/shear for few minutes (from about 5 to about 7 minutes). (Alternatively, they could be mixed for from about 5 to 30 minutes, depending upon the quantity of fuel being produced.)

[0100] In another beaker, the glycol (7.0%) was blended with the water (19.0%) and mixed at low/medium speed/shear for a few minutes. (Alternatively, depending upon the quantity being produced, it may be mixed from about 1 to about 20 minutes). Twenty percent in weight of the water/glycol blend was added to the pyrolysis oil/surfactant blend while stirring with a mixer at medium/high speed for few minutes (about 10 minutes, but it may alternatively be mixed from about 5 to about 30 minutes depending upon the quantity being produced). This is the hydration phase.

Slowly, allowing about 3 minutes for this addition, the remaining 80% of the water/glycol blend was added while increasing the rpm of the mixing process up to medium high speed/shear. The final emulsion was mixed for few minutes (for about 10 minutes). (Alternatively, the water/glycol blend may be added over about 1 to about 30 minutes, and then mixed for about 5 to about 45 minutes, depending upon the quantity of fuel being produced.)

[0102] The resulting fuel composition was tested for kinematic viscosity, gross heat of combustion (bomb calorimetry), pH, and pour point according to standard methods. The results are shown in Table 2.

<table>
<thead>
<tr>
<th>Test Description</th>
<th>Test Method</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kinematic Viscosity</td>
<td>ASTM D445</td>
<td>5.17 cSt</td>
</tr>
<tr>
<td>Gross Heat of Combustion</td>
<td>ASTM D240</td>
<td>35.01 MJ/Kg (15,054 btu/lb)</td>
</tr>
<tr>
<td>pH</td>
<td>ASTM E70</td>
<td>7.53</td>
</tr>
<tr>
<td>Pour Point</td>
<td>ASTM D6749</td>
<td>-59°C</td>
</tr>
</tbody>
</table>

The fuel composition was then successfully combined with 10% diesel, indicating that the emulsion was dispersible in diesel fuels.

Example 2

[0103] An oil in water emulsified biofuel was prepared including the components shown in Table 3 to produce 1000 g of the final fuel product. The crude pyrolysis oil used in this example was produced from a feedstock including a combination of post consumer plastic and paper.

<table>
<thead>
<tr>
<th>Material</th>
<th>Weight %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pyrolysis oil</td>
<td>72.49</td>
</tr>
<tr>
<td>Water</td>
<td>19.00</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>7.40</td>
</tr>
<tr>
<td>Chemax EM-1169</td>
<td>1.03</td>
</tr>
<tr>
<td>Tween 80</td>
<td>0.07</td>
</tr>
<tr>
<td>#2 Diesel fuel</td>
<td>0.10</td>
</tr>
</tbody>
</table>

[0105] A beaker was used having a simple impeller stirrer with a diameter equal to ⅓ of the diameter of the beaker. The main mix beaker was filled with the required amount of water. While mixing with the mixer, the required amount of ethylene glycol was added to the main mix beaker. The water and ethylene glycol were mixed using the mixer until the contents were well mixed, for about 3 minutes.

[0106] The required amount of #2 Diesel fuel was added to a secondary mixing beaker. Next, 30% of the pyrolysis oil was added to the secondary mixing beaker while mixing, and then 30% of the Chemax 1169 was added to the secondary mixing beaker while mixing. Mixing was continued until the contents were well mixed, for about 5 minutes. These steps were repeated with additional quantities of the pyrolysis oil and the Chemax 1169 being added to the secondary mixing beaker until only the final amount of each remained. The final amount the pyrolysis oil was then added to the secondary mix beaker. While mixing, the final amount of the Chemax 1169 was added to the secondary mix beaker. Next, again while mixing, the Tween 80 was added to the secondary mix beaker. Mixing was continued until the mixture was mixed, for about 10 minutes. This mixture was added to the main mix beaker while mixing with the mixer.
The combined contents were mixed in the main mixer until a stable emulsion was achieved. This required about 10 minutes. A color change of bright white/yellow was seen, indicating that a stable emulsion had formed. The final product was tested, and the lab results are shown in the table 4. The lower heat of combustion for this fuel product, as compared to the fuel product of Example 1, likely reflects the difference in the source materials used for producing the crude pyrolysis oil used in this example.

1. A fuel composition comprising:
- 50-90 wt % pyrolysis oil;
- 0.1-40 wt % water;
- 1-30 wt % alcohol; and
- 0.1-4 wt % surfactant;
wherein the composition is an emulsion.

2. The composition of claim 1 wherein the pyrolysis oil comprises crude pyrolysis oil.

3. The composition of claim 1 wherein the pyrolysis oil is produced by pyrolysis of biomass material.

4. The composition of claim 3 wherein the biomass comprises wood.

5. The composition of claim 1 wherein the alcohol comprises one or more polyalcohols or glycols.

6. The composition of claim 1 wherein the alcohol comprises propylene glycol or ethylene glycol.

7. The composition of claim 1 wherein surfactant comprises a non-ionic polymeric surfactant.

8. The composition of claim 7 wherein the surfactant is selected from the group consisting of Hypermer 1083SF, Monoamine ADD, Incromide, Chemax EM-1160, and Tween 80.

9. The composition of claim 1 further comprising a co-surfactant.

10. The composition of claim 9 wherein the surfactant comprises Hypermer 1083SF and the co-surfactant comprises Monoamine ADD or Incromide.

11. The composition of claim 9 wherein the surfactant comprises Chemax EM-1160 and the co-surfactant comprises Tween 80.

12. The composition of claim 1 further comprising diesel fuel.

13. The composition of claim 1 wherein the pyrolysis oil and surfactant form a continuous phase and the water and alcohol form a dispersed phase of the emulsion.

14. The composition of claim 1 wherein the water and alcohol form a continuous phase and the pyrolysis oil and surfactant form a dispersed phase of the emulsion.

15. A fuel composition emulsion comprising:
- a first phase comprising water and alcohol; and
- a second phase comprising pyrolysis oil and surfactant;
wherein one of the first and second phases forms a continuous phase and the other of the first and second phases forms a dispersed phase.

16. A method of forming a stable pyrolysis oil based fuel emulsion comprising:
- combining water and alcohol to form a water and alcohol mixture;
- separately combining pyrolysis oil and a surfactant to form a pyrolysis oil and surfactant mixture;
- adding a first portion of the water and alcohol mixture to the pyrolysis oil and surfactant mixture and mixing;
- adding a second portion of the water and alcohol mixture to the pyrolysis oil and surfactant mixture; and
- mixing until a stable emulsion is formed.

17. The method of claim 16 wherein the first and second portions of the water and alcohol mixture are formed together when the water and alcohol mixture is formed, and dividing the mixture into the first and second portions.

18. The method of claim 16 wherein the first and second portions of the water and alcohol mixture are made separately by combining a first quantity of water and a first quantity of alcohol to form the first portion and by combining a second quantity of water and a second quantity of alcohol to form the second portion.

19. The method of claim 16 wherein the surfactant is selected from the group consisting of Hypermer 1083SF, Monoamine ADD, Incromide, Chemax EM-1160, and Tween 80.

20. A method of forming a stable pyrolysis oil based fuel emulsion comprising:
- combining water and alcohol to form a water and alcohol mixture;
- separately combining pyrolysis oil and a surfactant to form a pyrolysis oil and surfactant mixture;
- adding a first portion of the pyrolysis oil and surfactant mixture to the water and alcohol mixture and mixing;
- adding a second portion of the pyrolysis oil and surfactant mixture to the water and alcohol mixture; and
- mixing until a stable emulsion is formed.

* * * * *

**TABLE 4**

<table>
<thead>
<tr>
<th>Method</th>
<th>Test</th>
<th>Result</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM D4052</td>
<td>Density of Liquids by Digital</td>
<td>0.9879</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Density Meter Relative Density at 15.56°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASTM D2709</td>
<td>Bottom water and sediment - stability test by centrifuge</td>
<td>&lt;0.05%</td>
<td></td>
</tr>
<tr>
<td>ASTM D93</td>
<td>Pensky-Martens Closed Cup Flash Point (Corrected Flash Point)</td>
<td>&gt;210°F</td>
<td></td>
</tr>
<tr>
<td>ASTM D445</td>
<td>Kinematic/Dynamic Viscosity</td>
<td>4.94</td>
<td>cP</td>
</tr>
<tr>
<td></td>
<td>Kinematic viscosity at 104°F/40°C</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ASTM D240</td>
<td>Heat of Combustion by Bomb</td>
<td>28.91</td>
<td>MJ/kg</td>
</tr>
<tr>
<td></td>
<td>Calorimeter Gross</td>
<td>(12,431)</td>
<td>btu/lb</td>
</tr>
<tr>
<td>ASTM D97</td>
<td>Pour Point of Petroleum</td>
<td>~24°C</td>
<td>(41.2°F)</td>
</tr>
<tr>
<td></td>
<td>Products/Pour Point</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Digital pH meter</td>
<td>pH at 20°C</td>
<td>5.7</td>
<td></td>
</tr>
</tbody>
</table>

* * * * *