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(54) **A MODIFIED EMULSIFIED FUEL OIL AND ITS PREPARATION METHOD**

(57) Taught is a modified emulsified fuel oil and its preparation method, prepared by mixing the below materials in weight percentage: heavy oil 40-50 wt%; softened water 10-25 wt%; emulsifier 0.1-0.5 wt%; light oil 5-30 wt%; modifier 1-15 wt%; and auxiliary agent 7.5-15

wt%. The heating value of said modified emulsified fuel oil is 8000-13000 kJ/kg. The emulsified fuel oil can be used for high-speed diesel engine trucks and fuel boilers.

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Description

[0001] The present invention relates to modified emulsified fuel oil and a method of its production.

[0002] The technology for emulsification of heavy oil has been researched for decades as emulsified fuel oil offers higher energy content and lower environmental impact. Many research institutes and chemical enterprises around the world commit significant funds in researching and developing this technology. More than \$5 billion has been spent in America to tackle and improve the technology. However, there are still many deficiencies to be improved, and thus one cannot promote the emulsification technology more widely.

[0003] The main deficiencies of the emulsified fuel oil are: 1) the storage is not stable, oil and water separation phenomena will happen in several months after emulsification, even only after several days; 2) the heating value reduces when burning, the heating value of a normal emulsification oil reduces to about 6000-7000 kcal/kg; 3) the sulfur content is not decreased significantly, especially for the oil emulsified from the heavy oil imported from middle east regions, the sulfur content is still more than 2%, resulting in the discharge of harmful gases such as SO₂, NO_x, soot, and so on, leading to serious environmental pollution; 4) the condensation point is high, the emulsification oil must be stored in an environment with a certain temperature; some emulsification oil can only be emulsified and then burned directly, and is unlike 0# light diesel oil that can be stored in oil storage tank and transported by pipelines; 5) the quality of emulsification oil is not improved largely, and thus can not be used for high speed diesel engines (>2200 rpm), agricultural transportation vehicles, and truck power units; 6) the ash content is high, the residual carbon and rare elements such as V and Mo are high, resulting in damage of the machines; and 7) the viscosity is high and a lot of colloids exist, resulting in jam of the nozzle.

[0004] A Chinese Patent with application number CN1329132 discloses a high-energy liquid fuel, comprising emulsified fuel oil and other auxiliary agents. However, the high energy liquid fuel cannot solve the above problems. For example, the storage stability is poor, the oil will thicken after storing for only 6 months; the sulfur content is certainly improved, but it still cannot meet the relevant national and international standards; though the condensation point is decreased, it is still not satisfying; the quality of the emulsification oil is increased and can meet the standard of 1# marine fuel oil, but it cannot satisfy the requirement of 0# light diesel fuel oil and thus cannot be used for high-speed diesel engine and tractor trucks; since the oil thickens after a certain time of storage, it cannot be transported by pipelines; and the raw materials to be used are also limited.

[0005] Therefore, a novel modified emulsified fuel oil having the advantages of stable storage, high heating value, low sulfur content, low condensation point, high quality, low ash content, and so on, is required urgently.

[0006] It is an objective of the present invention to provide a modified emulsified fuel oil prepared by mixing below materials in weight percentage: heavy oil 40-50 wt%; softened water 10-25 wt%; emulsifier 0.1-0.5 wt%; light oil 5-30 wt%; modifier 1-15 wt%; and auxiliary agent 7.5-15 wt%. The heating value of the modified emulsified fuel oil is 8000-13000 kJ/kg.

[0007] In a preferred embodiment of the present invention, the emulsified fuel oil is prepared by the steps of:

[0008] 1) heating 40-50 wt% heavy oil based on the overall weight of emulsified fuel oil to 80-90 °C in a preheating still;

[0009] 2) introducing 10-25 wt% H₂O into a reaction still and heating to 80-90 °C, then introducing 0.1-0.5 wt% emulsifier, based on the overall weight of emulsified fuel oil, into the reaction still and mixing;

[0010] 3) pumping the preheated heavy oil in the preheating still into the reaction still for mixing and emulsifying;

[0011] 4) based on the overall weight of emulsified fuel oil, introducing 5-30 wt% light oil, 1-15 wt% modifier, and 7.5-15 wt% auxiliary agent into the reaction still;

[0012] 5) shear mixing the materials in the reaction still under the rotating speed of 8000-15000 rpm, preferably 10000-13000 rpm, and temperature of 50-85 °C, preferably 55-75 °C, for 20 minutes to 10 hours, preferably 30 minutes to 5 hours, to obtain the product;

[0013] 6) feeding the product from step 5) into an aging tank to age 6-100 hours, preferably 24-100 hours, under the temperature of 45-75 °C, preferably, 50-60 °C to obtain the final product, namely the emulsified fuel oil.

[0014] In another preferred embodiment of the present invention, the heavy oil is one or more of 180# heavy oil and 250# heavy oil, the content of the heavy oil is 42-48wt%, preferably 45wt%, based on the overall weight of the emulsified fuel oil.

[0015] In another preferred embodiment of the present invention, the softened water is selected from water with water hardness of 7 or below, preferably 1-6, the content of the softened water is 15-20 wt%, preferably 18 wt%, based on the overall weight of the emulsified fuel oil.

[0016] In another preferred embodiment of the present invention, the emulsifier is one or more of the TG306 emulsifier and OP emulsifier, the content of the emulsifier is 0.1-0.15 wt%, preferably 0.13 wt%, based on the overall weight of the emulsified fuel oil.

[0017] In another preferred embodiment of the present invention, the light oil is one or more of the 0# light diesel oil, aviation fuel, 200# petroleum solvent, 1# marine fuel oil and 2# marine fuel oil, the content of the light oil is 10-25 wt%, preferably 20 wt%, based on the overall weight of the emulsified fuel oil.

[0018] In a preferred embodiment of the present invention, the modifier is one or more of the 200 # petroleum solvent and gasoline, the content of the modifier is 4-10 wt%, preferably 6 wt%, based on the overall weight of the emulsified fuel oil.

[0019] In a preferred embodiment of the present invention, the auxiliary agent is one or more of the detergent dispersant, condensing agent, combustion improver, and high energy agent, and preferably one or more of the isooctyl nitrate, isobutyl alcohol, polyetheramine, diisomyl oxalate, butylated hydroxytoluene, ethylene glycol monomethyl ether, water in oil emulsifier, polybutylene polyamide, tetraborane, and lithium aluminum hydride; the content of the auxiliary agent is 12-14 wt%, preferably 13 wt%, based on the overall weight of the emulsified fuel oil.

[0020] In accordance with the present invention, it is another objective of the present invention to provide a method for preparing the emulsified fuel oil, comprising the steps of:

[0021] 1) heating 40-50 wt% heavy oil based on the overall weight of emulsified fuel oil to 80-90 °C in a preheating still;

[0022] 2) based on the overall weight of emulsified fuel oil, introducing 10-25 wt% H₂O into a reaction still and heating to 80-90°C, then introducing 0.1-0.5 wt% emulsifier into the reaction still and mixing;

[0023] 3) pumping the preheated heavy oil in the preheating still into the reaction still for mixing and emulsifying;

[0024] 4) introducing 5-30 wt% light oil, 1-15 wt% modifier, and 7.5-15 wt% auxiliary agent into the reaction still;

[0025] 5) shear mixing the materials in the reaction still under the rotating speed of 8000-15000 rpm, preferably 10000-13000 rpm, and temperature of 50-85°C, preferably 55-75°C, for 20 minutes to 10 hours, preferably 30 minutes to 5 hours, to obtain the product;

[0026] 6) feeding the product from step 5) into an aging tank to age 6-100 hours, preferably 24-100 hours, under the temperature of 45-75°C, preferably, 50-60°C to obtain the final product, namely the emulsified fuel oil.

[0027] In certain embodiment of the present invention, the application of the mixture comprising 40-50 wt% heavy oil, 10-25 wt% softened water, 0.1-0.5 wt% emulsifier, 5-30 wt% light oil, 1-15 wt% modifier, and 7.5-15 wt% auxiliary agent in the preparation process of emulsified fuel oil is also provided.

[0028] As a result, the method of the present invention makes the most of the valuable energy resources and cheap materials, changes waste into values, improves oil quality, and converts emulsified fuel oil of low heating value, high viscosity, high sulfur content, water contained, and high condensation point into the emulsified fuel oil with the advantages of high heating value, low viscosity, good liquidity, low sulfur content, and low condensation point.

[0029] The emulsified fuel oil of the present invention can satisfy the technical standard of 0# light diesel oil, and thus can be used for high speed diesel engine trucks and fuel boiler, and can be burnt completely without discharging dark smoke, and thereby, reaches the standard of environmental protection and energy saving. The emulsified fuel oil of the present invention can be stored for a long time without layering and contains particles with a particle size of less than 5 μm, and has a good liquidity under the temperature of between -20°C and -40°C, and thus can be stored and transported conveniently.

[0030] As one objective of the present invention, there is provided a modified emulsified fuel oil, prepared by mixing below materials in weight percentage: heavy oil 40-50 wt%; softened water 10-25 wt%; emulsifier 0.1-0.5 wt%; light oil 5-30 wt%; modifier 1-15 wt%; and auxiliary agent 7.5-15 wt%. The heating value of the modified emulsified fuel oil is 8000-13000 kJ/kg.

[0031] Generally, the modified emulsified fuel oil is mixed formed by the below materials in weight percentage: heavy oil 40-50 wt%, preferably 42-48 wt%, and more preferably 45 wt%; softened water 10-25 wt%, preferably 15-20 wt%, and more preferably 18 wt%; emulsifier 0.1-0.5 wt%, preferably 0.1-0.15 wt%, and more preferably 0.13 wt%; light oil 5-30 wt%, preferably 10-25 wt%, and more preferably 20 wt%; modifier 1-15 wt%, preferably 4-10 wt%, and more preferably 6 wt%; auxiliary agent 7.5-15 wt%, preferably 12-14 wt%, and more preferably 13 wt%.

[0032] In the present invention, the heavy oil is made by decreasing the viscosity of the residual oil obtained from the atmospheric vacuum distillation of the raw oil or introducing proper other distillate oil into or secondary hot working on the residual oil. In the present fields, the heavy oil generally means one or more of the 180# heavy oil or 250# heavy oil. In a preferred embodiment of the present invention, the heavy oil is 180# heavy oil. In another preferred embodiment of the present invention, the heavy oil is 250# heavy oil. In another preferred embodiment of the present invention, the heavy oil is the mixture of the 180# heavy oil and 250# heavy oil.

[0033] In the emulsified fuel oil of the present invention, the content of the heavy oil is 40-50 wt%, preferably 42-48 wt%, and more preferably 45 wt%, based on the overall weight of the emulsified fuel oil.

[0034] In the present invention, the softened water has a hardness of 7 or below, namely the content of calcium carbonate is below 50 ppm, preferably 15-50 ppm. The softened water can be made by a normal softening method to soften the city water. The softening method includes normal distillation, ion exchange, and so on. In a preferred embodiment of the present invention, the softened water is city water processed by ion exchange resin having a hardness of 1-6, preferably 2-4, and more preferably 3.

[0035] In the present invention, besides softened water, hard water, such as normal city water, river water, well water, can also be used. Since the hard water contains a large amount of metal ions such as Ca²⁺, Mg²⁺, and so on, the production and application of the emulsified fuel oil is limited, for example, it may corrode the production equipments, or scale in the engine or reaction still. Therefore, using softened water in the present invention is preferred.

[0036] In the emulsified fuel oil of the present invention, the content of the softened water is 10-25 wt%, preferably 15-20 wt%, and more preferably 18 wt%, based on the overall weight of the emulsified fuel oil.

[0037] In the present invention, the light oil is based on a distillate obtained by the atmospheric vacuum distillation of the raw oil under certain temperature and secondary processed diesel oil mixed under a certain ratio. In the present invention, the light oil is normal, and can be selected based on the type and quantity of the heavy oil as long as the purpose of the present invention can be reached. In a preferred embodiment of the present invention, the light oil is one or more of the 0# light diesel, aviation fuel, 200# petroleum solvent, 1# marine fuel oil and 2# marine fuel oil.

[0038] In the emulsified fuel oil of the present invention, the content of the light oil is 5-30 wt%, preferably 10-25 wt%, and more preferably 20 wt%, based on the overall weight of the emulsified fuel oil.

[0039] In the present invention, the emulsifier can be any normal emulsifier (such as water in oil emulsifier or oil in water emulsifier) or their mixture. In a preferred embodiment of the present invention, the emulsifier is one or more of the G306 emulsifier and OP emulsifier, wherein TG306 emulsifier is preferred.

[0040] In the emulsified fuel oil of the present invention, the content of the emulsifier is 0.1-0.5 wt%, preferably 0.1-0.15 wt%, and more preferably 0.13 wt%, based on the overall weight of the emulsified fuel oil.

[0041] In the present embodiment, the modifier can be a normal modifier in the present field as long as it can change the liquidity of the emulsified fuel oil of the present invention. In a preferred embodiment of the present invention, the modifier is one or more of the 200# petroleum solvent and gasoline, wherein gasoline is preferred.

[0042] In the emulsified fuel oil of the present invention, the content of the modifier is 1-15 wt%, preferably 4-10 wt%, and more preferably 6 wt%, based on the overall weight of the emulsified fuel oil.

[0043] In the present embodiment, the auxiliary agent is a normal auxiliary agent in the present field and is one or more of the detergent dispersant, condensing agent, combustion improver, and high energy agent. In an embodiment of the present invention, the auxiliary agent is one or more of the isooctyl nitrate, isobutyl alcohol, polyetheramine, diisoamyl oxalate, butylated hydroxytoluene, ethylene glycol monomethyl ether, water in oil emulsifier, polybutylene polyamide, tetraborane, and lithium aluminum hydride.

[0044] In the emulsified fuel oil of the present invention, the total content of the auxiliary agent is 7.5-15 wt%, preferably 12-14 wt%, and more preferably 13 wt%, based on the overall weight of the emulsified fuel oil, wherein the content of each auxiliary agent is 0.05-10 wt%, preferably 0.1-5 wt%.

[0045] In the present invention, the content of various auxiliary agents can be selected specifically according to the property of the emulsified fuel oil, which is well known to those skilled in the art, as long as the total amount of the auxiliary agents is within the content range of the auxiliary agents. In a preferred embodiment of the present invention, the content of the isooctyl nitrate is 0.1-3 wt%, preferably 0.5-2 wt%; the content of the diisoamyl oxalate is 0.5-3 wt%, preferably 1-2 wt%; the content of the tetraborane is 1.5-3 wt%, preferably 1.87-2 wt%; the content of the polybutylene polyamide is 0.5-3 wt%, preferably 1-2 wt%; the content of the ethylene glycol monomethyl ether is 0.5-3 wt%, preferably 1-2 wt%; the content of the butylated hydroxytoluene is 0.5-3 wt%, preferably 1-2.2 wt%, based on the overall weight of the emulsified fuel oil.

[0046] In the emulsified fuel oil of the present invention, various additives can be added according to demand as long as they do not influence the performance of the emulsified fuel oil. For example, the additive is one or more of the pigments and thinners (such as isobutyl alcohol). The content of the additive is random as long as it does not have bad influence on the performance of the emulsified fuel oil. In a preferred embodiment of the present invention, the content of the additive is 0.1-10 wt%, preferably 0.5-7 wt%, and more preferably 1-5 wt%, optimally 2 wt%, based on the overall weight of the emulsified fuel oil.

[0047] In the present invention, the heating value of the emulsified fuel oil is 8000-13000 kJ/kg, preferably 10000-13000 kJ/kg, and more preferably 11000 kJ/kg.

[0048] As another objective of the present invention, there is provided a method for preparing the emulsified fuel oil of the present invention, comprising the steps of:

[0049] 1) heating 40-50 wt% heavy oil based on the overall weight of emulsified fuel oil to 80-90 °C in a preheating still;

[0050] 2) introducing 10-25 wt% H₂O into a reaction still and heating to 80-90°C, then introducing 0.1-0.5 wt% emulsifier into the reaction still and mixing;

[0051] 3) pumping the preheated heavy oil in the preheating still into the reaction still for mixing and emulsifying;

[0052] 4) based on the overall weight of emulsified fuel oil, introducing 5-30 wt% light oil, 1-15 wt% modifier, and 7.5-15 wt% auxiliary agent into the reaction still;

[0053] 5) shear mixing the materials in the reaction still under the rotating speed of 8000-15000 rpm, preferably 10000-13000 rpm, and temperature of 50-85°C, preferably 55-75°C, for 20 minutes to 10 hours, preferably 30 minutes to 5 hours, to obtain the product;

[0054] 6) feeding the product from step 5) into an aging tank to age 6-100 hours, preferably 24-100 hours, under the temperature of 45-75°C, preferably, 50-60°C to obtain the final product.

[0055] In step 5), the temperature is preferably 60°C.

[0056] In step 5), the reaction still can be fully closed, semi-closed, or open. In order to avoid the introduction of

impurities, the reaction still is preferably fully closed or semi-closed.

[0057] In step 2), the reaction still is preferably installed with a high shearing emulsification pump, a static mixer, and a high-speed disperser.

[0058] In step 4), the introduction sequence of the light oil, modifier, and auxiliary agent is random. In a preferred embodiment of the present invention, the introduction sequence of the materials is light oil, modifier, and auxiliary agent.

[0059] Though the reaction still equipped with a high shearing emulsification pump, a static mixer, and a high-speed disperser can be used in the present invention. Other reaction still equipped with other mixing equipments can also be selected according to demand by normal technicians in the present field, as long as the materials inside of the reaction still can be emulsified completely under the proper reaction conditions, in order to realize the purpose of the present invention.

[0060] In a preferred embodiment of the present invention, the reaction time is 1-4 hours, and more preferably 2 hours.

[0061] In a preferred embodiment of the present invention, the aging time is 36-72 hours, and more preferably 48 hours.

[0062] The emulsified fuel oil of the present invention provides the advantages of:

[0063] 1) high total heating value, which is up to 13000kJ/kg;

[0064] 2) low sulfur content, which reduces the discharge of SO₂, NO_x and soot, and thus can satisfy environmental protection standard;

[0065] 3) low condensation point, which can be used under a temperature of 40°C;

[0066] 4) high storage stability, which can be stored for 2 years without any layering;

[0067] 5) fully utilization on energy resources, which can change wastes into valuables;

[0068] 6) low kinematics viscosity, which allows the modified emulsified fuel oil to be transported by pipelines;

[0069] 7) high fuel utilization rate, which is increased two levels and thus can be used for high-speed diesel engines; and

[0070] 8) complete combustion, which is free of influence on the performance of equipments.

[0071] The emulsified fuel oil of the present invention is mainly used as a substitute for diesel oil, heavy oil, coal oil, and so on, and is suitable for using in ceramic factory, glass factory, SiC factory, metal smelting factory, fuel power factory, steamboat, watercraft, high-, middle-, and low-speed diesel engine, fuel boiler, fuel cooking utensils, agricultural tractor, truck, and so on.

[0072] The application method of the modifier emulsified fuel oil of the present invention is the same as that of the 0# light diesel, the mechanical structure of the engine does not need to be improved. The modified emulsified fuel oil of the present invention can be stored in oil tank without any heat preservation effort.

[0073] Since the content of sulfur and other rare elements (such as V, Mo, Ni, etc) content in the emulsified fuel oil of the present invention is low, the mechanical parts of engines driven by it are not corroded and worn out easily.

[0074] The technology being used for preparing modified emulsified fuel oil of the present invention offers a low investment on fixed equipment, has a simple process, can be applied to mass production, and do not have three wastes pollution. Generally, the investment on the fixed equipment required by the technology of the present invention is 10% of oil refinery factory.

[0075] The present invention will hereinafter be described in detail based on the specific embodiments. It should be understood that these embodiments can only be used for describing the present invention, and can not limit the range of the present invention. The experimental methods without giving a clear indication of conditions in below embodiments generally follow normal conditions or conditions suggested by the manufacturer.

[0076] EXAMPLES

[0077] General method:

[0078] Physical and chemical parameter test of fuel oil

[0079] The various physical and chemical parameters of the modified emulsified fuel oil of the present invention were tested by Zhejiang Fangyuan test group according to the standards of GB/T260 determination of water of petroleum products, GB/T261 determination of flash point of petroleum products (closed up method), GB/T265 determination of kinematic viscosity and dynamic viscosity of petroleum products, GB/T380 determination of sulfur content of petroleum products (lamp method), GB/T384 determination of heating value of petroleum products, GB/T508 determination of ash content of petroleum products, GB/T510 determination of condensation point of petroleum products, GB/T1848 determination of density of petroleum and petroleum products (densimeter method), GB/T4756 sampling method of petroleum and petroleum products, GB/T5096 Test for copper strip corrosion of petroleum products, GB/T package, storage, and transportation rules of petroleum products.

[0080] Discharge test

[0081] The various discharge results of the modified emulsified fuel oil of the present invention were tested by Zhejiang environment monitoring center according to the standard of GB/T16157-1996, Determination of particulates and sampling methods of gaseous pollutants emitted from exhaust gas of stationary source.

[0082] Dynamic performance of fuel oil by bench test method

[0083] The dynamic performance of the modified emulsified fuel oil of the present invention was tested by energy utilization monitoring center of Wuhan Yangtze river navigation research institute according to the standard of

GB/T6072.0-2000 Reciprocating internal combustion engines - Performance - Part 1: Declarations of power, fuel and lubricating oil consumptions, and test methods.

[0084] Safety test

[0085] The safety performance of the modified emulsified fuel oil of the present invention was tested by Zhejiang chemical product quality inspection station according to hazard assessment of explosion, hazard assessment of oxidizer, hazard assessment of flammability, hazard assessment of corrosion, hazard assessment of toxicity, hazard assessment of radiation, and hazard assessment of other performance.

[0086] Storage performance test

[0087] Storing the modified emulsified fuel oil of the present invention under temperature of 25°C for 1 month, 6 months, 1 year, and 2 years, respectively to inspect the layering performance.

[0088] Example 1

[0089] Introduced 20 kg 250# heavy oil and 180# heavy oil (imported from Korea) into the preheating still (purchased from Jiangsu qidong chemical equipment factory), heated the preheating still to 90°C and held the preheating still at this temperature.

[0090] Introduced 16.4 kg softened water (hardness is 3) into the reaction still (purchased from Jiangsu Qidong chemical equipment factory) equipped with a high shearing emulsification pump, a static mixer, and a high-speed disperser, and heated it to 90°C, then introduced 0.1 kg of TG306 emulsifier (purchased from Tianjin energy technology research institute) and mixed.

[0091] Pumped the preheated heavy oil from the preheating still to the reaction still for mixing and emulsifying. Introduced orderly 10 kg 0# light diesel, 10 kg 260 aviation fuel and 1 kg 1#fuel oil (purchased from China petroleum group), 4.3 kg dynamic benzene (purchased from Hangzhou oil refinery factory), 2 kg isooctyl nitrate (purchased from Shandong petrochemicals complex), 2 kg diisoamyl oxalate (Nanjing Hengan resin plant), 2 kg tetraborane (B_4H_{10}) (purchased from Lanzhou oil refinery chemical factory), 2 kg polybutylene polyamide (purchased from Lanzhou oil refinery chemical factory), 2 kg ethylene glycol monomethyl ether (purchased from Shanghai No.3 reagent plant) and 2.2 kg butylated hydroxytoluene (purchased from Shanghai Xiangyang chemical plant) into the reaction still.

[0092] Started up the high-shearing emulsification pump, static mixer and high-speed disperser, emulsified the materials in the reaction still in a fully closed status under rotation speed of 11000 rpm and temperature of 60°C for 60 minutes.

[0093] Outputted the obtained product from reaction still to the aging tank so as to get the modified emulsified fuel oil after 24 hours aging.

[0094] Examples 2-4

[0095] Using the same method as in Example 1 to prepare modified emulsified fuel oil, the material content and preparation conditions are shown in Table 1.

Table 1 Material content and preparation conditions for the modified emulsified fuel oil of the present invention

	Example 2	Example 3	Example 4
250# heavy oil	20	0	43
180# heavy oil	30	45	0
Softened water (hardness is 3)	25	22.5	19.35
TG306 emulsifier	0.13	0.12	0.12
0# light diesel	8	10	11
260 aviation fuel	3.8	5.5	0
Lamp kerosene	0	0	6
1# fuel oil	0	4.88	8.03
Dynamic benzene	5.2	4.5	4.5
isooctyl nitrate	0.5	0.5	0.5
diisoamyl oxalate	1	1	1.5
tetraborane	1.87	2	2
polybutylene polyamide	2	1	1
ethylene glycol monomethyl ether	1	2	2
butylated hydroxytoluene	1.5	1	1

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(continued)

	Example 2	Example 3	Example 4
Temperature of preheating still and reaction still, °C	85	80	88
Reaction time, hr	2	3	4
Aging time, hr	36	72	96

[0096] Example 6

[0097] Doing the physical and chemical parameter test, discharge test, dynamic performance test, safety test, and storage performance test for the products obtained from Example 1 to Example 4, the results are shown in Table 2:

Table 2 the physical and chemical parameters of emulsified fuel oil from example 1 and 0# light diesel oil

Project	Total heating value_KJ/KG	Sulfur content %	Residual carbon %	Ash content %	Mechanical impurities	Water content %	Closed flash point	Copper strip corrosion 50°C	Density 20°C g/m ³	Kinematic viscosity 50°Cmm ³ /s	Condensation point °C	Cetane
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Example 1	10611.6	0.22	0.05	0.006	0.02	trace	38°C	< 1	0.855	5.5	-41	53
0# light diesel oil	9700	0.2	0.3	0.1	None	trace	55°C	1	0.820-0.840	3-8	0	45

[0098] The test results for the physical and chemical parameters of emulsified fuel oil of Example 2 to Example 4 are similar to those of Example 1, its total heating value is in the range of 9600-11000 kJ/kg, and its condensation point is -35°C and -42°C, respectively. It is clear that the emulsified fuel oil of Example 1 to Example 4 has high combustion heating value and nice cold resistance performance.

Table 3 Discharge test results of emulsified fuel oil of example 1 and relevant permitted discharge concentration

Test items	Soot discharge concentration	SO ₂ discharge concentration	NO _x discharge concentration	Smoke blackness
Example 1	71.8 mg/m ³	162.3 mg/m ³	264.7 mg/m ³	< grade 1
Permitted discharge concentration	100 mg/m ³	(coal, diesel oil) 700 mg/m ³	400 mg/m ³	Grade 1

[0099] The discharge test results for emulsified fuel oil of Example 2 to Example 4 are similar to those of example 1, and are within the range of permitted discharge standard.

Table 4 Dynamic test results of emulsified fuel oil of example 1 and 0# diesel oil

	Diesel engine can be operated normally?	Obvious change on dynamics?	Percentage of oil consumption compared to 0# light diesel
Example 1	Yes	No	105 %
Example 2	Yes	No	106 %
Example 3	Yes	No	107 %
Example 4	Yes	No	104 %

Table 5 Hazard assessment results of emulsified fuel oil of example 1

Explosion hazard assessment	Multiple solicitation test: no explosion and deflagration hazard, presenting that the emulsified fuel oil does not belong to explosion hazard material
Oxidization hazard assessment hazard	Oxidization test: No severe reaction, presenting that the emulsified fuel oil does not belong to oxidant hazard material.
Flammability hazard assessment	Fire and flame ignition test: flammable under open flame Flash point (closed cup): 38°C Auto-ignition test: No heating, auto-burning Water resistant test: no flammable gas discharged, presenting that the emulsified fuel oil belongs to flammable hazard material
Corrosion hazard assessment	Touch test: no visible damage to skin and test material, presenting that the emulsified fuel oil does not belong to corrosion hazard material
Toxicity hazard assessment	Records show that the emulsified fuel oil does not belong to toxicity hazard material
Radiation hazard assessment	Records show that the emulsified fuel oil has a radioactivity ratio of <74 KBg/kg
Other hazard assessment	Other hazard test: no feter, no infectious substance, presenting that the emulsified fuel oil does not belong to other hazard material

[0100] The safety test results of emulsified fuel oil of Example 2 to Example 4 is similar to those of example 1, besides flammability hazard, the emulsified fuel oil does not have other hazard.

Table 6 the storage performance of emulsified fuel oil of the present invention

	1 month	6 months	1 year	2 years
Example 1	Free of layering	Free of layering	Free of layering	Free of layering
Example 2	Free of layering	Free of layering	Free of layering	Free of layering
Example 3	Free of layering	Free of layering	Free of layering	Free of layering
Example 4	Free of layering	Free of layering	Free of layering	Free of layering

[0101] Example 7

[0102] Applying the emulsified fuel oils of example 1 to example 4 to the agricultural tractor (truck), big fuel boiler, oil tanker, and fisher, respectively, for one month, the results turned out that the emulsified fuel oils of Example 1 to Example 4 have good performance on oil saving, soot discharge, dynamic operation, torque, and so on.

[0103] Although the present invention has been described in connection with preferred embodiments thereof, it will be appreciated by those skilled in the art that additions, modifications, substitutions and deletions not specifically described may be made without departing from spirit and scope of the invention as defined in the claims.

Claims

1. A modified emulsified fuel oil, prepared by mixing following materials in following weight percentages:

heavy oil, 40-50 wt%;
softened water, 10-25 wt%;
emulsifier, 0.1-0.5 wt%;
light oil, 5-30 wt%;
modifier, 1-15 wt%; and auxiliary agent, 7.5-15wt%;

wherein,
said modified emulsified fuel oil has a heating value of between 8000 and 13000 kJ/kg.

2. The fuel oil of claim 1, wherein said emulsified fuel oil is prepared by the steps of:

a) heating 40-50 wt% of said heavy oil based on the overall weight of the modified emulsified fuel oil to 80-90°C in a preheating still;
b) introducing 10-25 wt% of said H₂O based on the overall weight of the modified emulsified fuel oil into a reaction still and heating to 80-90 °C, then introducing 0.1-0.5 wt% emulsifier based on the overall weight of the modified emulsified fuel oil into the reaction still and mixing;
c) pumping said preheated heavy oil from the preheating still into the reaction still for mixing and emulsifying;
d) introducing 5-30 wt% light oil based on the overall weight of the modified emulsified fuel oil, 1-15 wt% modifier based on the overall weight of the modified emulsified fuel oil, and 7.5-15 wt% auxiliary agent based on the overall weight of the modified emulsified fuel oil into the reaction still;
e) shear mixing contents of the reaction still under the rotating speed of 8000-15000 rpm, preferably 10000-13000 rpm, at a temperature of 50-85°C, preferably 55-75°C, for a time period between 20 minutes and 10 hours, preferably 30 minutes to 5 hours, to obtain a final product,
f) feeding the product from step e) into an aging tank to age for a period of between 6 and 100 hours, preferably 24-100 hours, at a temperature of between 45 and 75°C, preferably 50-60°C, to obtain the final product, modified emulsified fuel oil.

3. The fuel oil of claim 1, wherein said heavy oil is one of 180# heavy oil or 250# heavy oil; and the weight percentage of said heavy oil based on the overall weight of said emulsified fuel oil is 42-48 wt%, preferably 45 wt%.

4. The fuel oil of claim 1, wherein said softened water is water having hardness of 7 or below, preferably between 1 and 6, the weight percentage of said softened water is 15-20 wt% based on the overall weight of said emulsified fuel oil, and preferably 18 wt%.

5. The fuel oil of claim 1, wherein said emulsifier is one or more of TG306 emulsifier and OP emulsifier, and the weight percentage of said emulsifier based on the overall weight of said emulsified fuel oil is between 0.1 and 0.15 wt%, and preferably 0.13 wt%.

6. The fuel oil of claim 1, wherein said light oil is selected from one or more of the group consisting of 0# light diesel oil, aviation fuel oil, 200# solvent, 1# marine fuel oil, and 2# marine fuel oil, and the content of said light oil based on the overall weight of said emulsified fuel oil is between 10 and 25 wt%, and preferably 20 wt%.

7. The fuel oil of claim 1, wherein said modifier is one or more of 200# petroleum solvent and gasoline, the content of said modifier based on the overall weight of said emulsified fuel oil is between 4 and 10 wt%, and preferably 6wt%.

8. The fuel oil of claim 1, wherein said auxiliary agent is selected from one or more of the group consisting of detergent dispersant, condensing agent, combustion improver, and high energy agent, and is preferably is selected from one or more of the group consisting of isooctyl nitrate, isobutyl alcohol, a polyetheramine, diisoamyl oxalate, butylated hydroxytoluene, ethylene glycol monomethyl ether, water in oil emulsifier, polybutylene polyamide, tetraborane, and lithium aluminum hydride; and the content of said auxiliary agent based on the overall weight of said emulsified fuel oil is between 12 and 14 wt%, and preferably 13 wt%.

9. A method of preparing the fuel oil of claim 1, comprising:

- a) heating 40-50 wt% of said heavy oil based on the overall weight of the modified emulsified fuel oil to 80-90 °C in a preheating still;
- b) introducing 10-25 wt% of said H₂O based on the overall weight of the modified emulsified fuel oil into a reaction still and heating to 80-90 °C, then introducing 0.1-0.5 wt% emulsifier based on the overall weight of the modified emulsified fuel oil into the reaction still and mixing;
- c) pumping said preheated heavy oil from the preheating still into the reaction still for mixing and emulsifying;
- d) introducing 5-30 wt% light oil based on the overall weight of the modified emulsified fuel oil, 1-15wt% modifier based on the overall weight of the modified emulsified fuel oil, and 7.5-15 wt% auxiliary agent based on the overall weight of the modified emulsified fuel oil into the reaction still;
- e) shear mixing contents of the reaction still under the rotating speed of 8000-15000 rpm, preferably 10000-13000 rpm, at a temperature of 50-85°C, preferably 55-75°C, for a time period between 20 minutes and 10 hours, preferably 30 minutes to 5 hours, to obtain a product;
- f) feeding the product from step e) into an aging tank to age for a period of between 6 and 100 hours, preferably 24-100 hours, at a temperature of between 45 and 75°C, preferably 50-60°C, to obtain the final product, modified emulsified fuel oil.

10. A mixture for preparing the emulsified fuel oil of claim 1, comprising:

heavy oil 40-50 wt%;
softened water 10-25 wt%;
emulsifier 0.1-0.5 wt%;
light oil 5-30 wt%;
modifier 1-15 wt%; and
auxiliary agent 7.5-15 wt%.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2006/001395

A. CLASSIFICATION OF SUBJECT MATTER

See extra sheet

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10L(2006.01)

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT, CNKI, WPI, EPODOC, PAJ: heavy oil, residual oil, residuum, emulsif+, modif+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CN1077481 A(ZHONG Jianguo) 20.Oct.1993(20.10.1993) Claim 1, Description,Page 2, last Line-Page3,Line 4	1-6,8,10
Y		7,9
Y	CN1329132 A(WANG Xianlun) 02.Jan.2002(02.01.2002) Claims 1-2	1-9
Y	CN1019130 B(DRILLING WELL & OIL PRODN ART) 18.Nov.1992(18.11.1992) Claims 2-3	1-9
A	JP59081386 A(NAOJIROU NEMOTO) 11.May.1984(11.05.1984)	1-10
A	JP57049696 A(NAITO AKIRA) 23.Mar.1982(23.03.1982)	1-10
A	US2002011022 A1(WOS NIJUICHI KK ET-AL) 31.Jan.2002(31.01.2002)	1-10

☐ Further documents are listed in the continuation of Box C.☒ See patent family annex.

* Special categories of cited documents:

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"document member of the same patent family

Date of the actual completion of the international search

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2006/001395

Patent Documents referred in the Report	Publication Date	Patent Family	Publication Date
CN1077481 A	20-10-1993	NONE	
CN1329132 A	02-01-2002	NONE	
CN1019130 B	18-11-1992	NONE	
JP59081386 A	11-05-1984	NONE	
JP57049696 A	23-03-1982	NONE	
US2002011022 A1	31-01-2002	KR2002009531 A	01-02-2002
		JP2002080872 A	22-03-2002

Form PCT/ISA /210 (patent family annex) (April 2005)

INTERNATIONAL SEARCH REPORT

International application No.

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CLASSIFICATION OF SUBJECT MATTER

C10L1/32(2006.01)i
C10L1/182(2006.01)n
C10L1/185(2006.01)n
C10L1/19(2006.01)n
C10L1/22(2006.01)n

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- CN 1329132 [0004]