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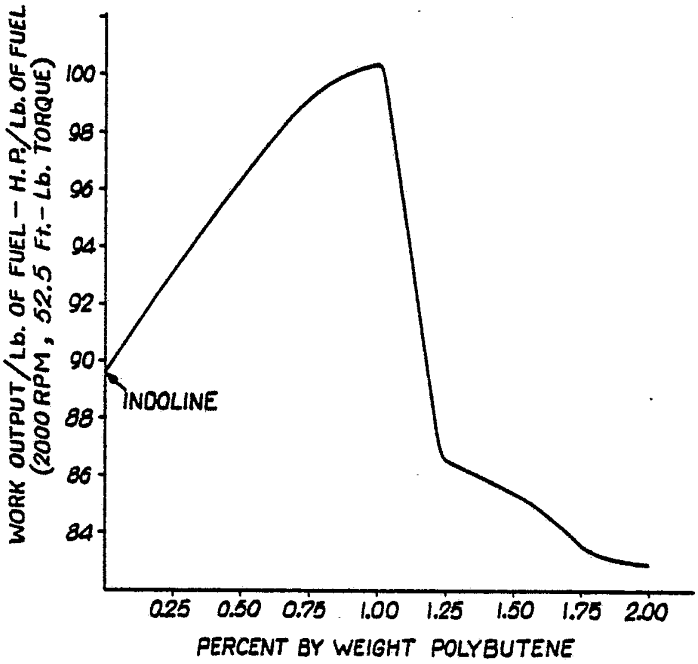
(54) Title: FUEL COMPOSITIONS

(57) Abstract

Improved fuels having significantly increased combustion efficiencies, desirable octane ratings and lowered polution emissions which are supplemented by a minor amount of a polyolefinic additive containing recurring C_2-C_{10} monomer moieties therein. The fuels preferably include a liquid hydrocarbon such as a gasoline or diesel fuel, with up to about 2.5% by weight polyolefin, or in certain cases a polyolefin derivative. The most preferred additive for use in the fuel of the invention is polybutene. Stable emulsified fuels are also provided which comprise respective fractions of water, liquid combustible hydrocarbon, one or more surfactants, and a polyolefin additive. Test results demonstrate that the fuels of the invention exhibit greater work output per pound of fuel than straight unmodified comparative fuels. The presence of polyolefins in the fuel is believed to generate reactions analogous to cracking during combustion of the fuel compositions, with the resultant exothermic heats of reaction adding substantially to the caloric values obtained from the fuels; in the case of emulsified fuels for example, this factor is believed to compensate for the potential caloric loss represented by the presence of significant amounts of water.



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FUEL COMPOSITIONS

Background of the Invention

1. Field of the Invention

The present invention is concerned with greatly improved fuel compositions having a number of desirable properties such as significantly increased combustion efficiencies so that the fuels are more economical in use. More particularly, it is concerned with such fuels which are supplemented by minor amounts of certain polyolefins or derivatives thereof; the fuels of the invention include typical hydrocarbon fuels such as gasoline or diesel fuel in combination with an appropriate polyolefin additive, and also emulsified fuels containing substantial fractions of water.

2. Description of the Prior Art

A vast number of additives have been proposed in the past for use with conventional hydrocarbon fuels such as gasoline, diesel fuel or the like. In many cases additives have been proposed to remedy specific problems, such as the elimination of knocking through the addition of tetraethyl lead to gasoline. Other agents have also been proposed for the purpose of enhancing combustion efficiency, and hence the work output derived per unit of fuel consumed.

Alas, while the prior art is replete with attempts at providing significant enhancement of combustion efficiency, few if any truly successful additives have been discovered.

Researchers in the art have also proposed that significant quantities of water could be added to liquid hydrocarbon fuels to form a combustible emulsion which would, theoretically, lessen the consumption of the expensive hydrocarbon fuel. Indeed, such proposals extend back to the late nineteenth century. Here again though, no truly successful fuel/water emulsion has been developed in the past. The numerous problems heretofore experienced with such emulsified fuels include the fact that, when relatively large quantities of water are present, the combustion temperature is lowered; moreover, the presence of substantial water lowers the overall caloric value of the fuel. Finally, many prior fuel/water emulsions are relatively unstable, and tend to separate over time. Of course, if large quantities of surfactants are employed in such emulsions, the problem of phase separation can be avoided; however, this is inherently a very expensive proposition, and therefore in order to be truly economical, the amount of surfactant employed in an emulsified fuel must be relatively small.

Patent No. 2,896,593 relates to a two cycle fuel which includes a mixture of lead-free, straight run gasoline and from about 6-9% by volume polyisobutylene. This combination is said to be particularly useful in two cycle engines, where the polyisobutylene prevents engine fouling.

Patent No. 3,753,905 is likewise directed to a two cycle fuel which includes polybutene along with mineral oil and other additives. Patent No. 3,085,978 is in some respects similar to the last mentioned patent, and teaches the use of polybutene along with a calcium salt of petroleum sulfonic acid in the context of a fuel composition.

Patents Nos. 3,909,214 and 3,782,912 describe the use of polyolefins as fuel additives, along with other constituents such as amine salts and the like. However, none of the above mentioned patents relate specifically to emulsified fuels.

Other patents of background interest include U.S. Patents Nos. 4,162,143, 2,642,345, 4,339,246, 2,356,647, 4,392,865, 2,920,948, 3,163,603, 3,451,931, 4,125,382, 2,873,182, 3,410,671, 2,959,551, 3,271,310, 3,783,131 and 3,779,922.

Summary of the Invention

It has now been discovered that greatly improved fuel compositions can be provided which overcome many of the intractable problems discussed above. Broadly speaking, the invention resides in the discovery that use of certain types of polyolefinic compounds, typically in relatively minor amounts, gives significantly enhanced combustion efficiencies.

In one aspect of the invention, an improved fuel essentially free of lubricating oil is provided. The fuel comprises (and preferably consists essentially of) a combustible hydrocarbon material, and up to about 2.5% (e.g., about 0.1-2.5%) by weight of a polyolefinic additive. The type and amount of additive serve to increase the work output per unit of fuel obtained using the improved fuel, as compared with the work output per unit of fuel obtained under the same conditions and using the identical fuel except for the absence of the polyolefinic additive therein. The additive is selected from the group consisting of polyolefins having recurring C_2-C_{10} monomers therein (i.e., the monomers contain from 2 to 10 carbon atoms, inclusive), and derivatives of such polyolefins.

In preferred forms, the hydrocarbon material is selected from the group consisting of liquid hydrocarbons such as the gasolines, diesel fuels and heavy fuel oils of virtually any specific composition and type. The polyolefinic additive (the most preferred polyolefin being polybutene or polyisobutylene) is advantageously present at a level of from about 0.1 to 2% by weight, and most preferably at a level of from about 0.3 to 0.8% by weight. However, those skilled in the art will recognize that the specific amount of polyolefinic additive to be employed in a particular situation depends upon the hydrocarbon base material being employed, and the desired characteristics in the ultimate polyolefin-supplemented fuel. For example, in the case of indoline it has been surprisingly discovered that good results are obtained when using polybutene at a level of up to about 1% (e.g., about 0.1-1%) by weight, but that significantly above this level of usage the results are dramatically reduced.

A wide variety of polyolefinic additives can be used in the context of the invention. While polyolefins having recurring C_2-C_{10} monomers can be used, the most preferred polyolefins have recurring C_3-C_6 monomers therein. In addition to the most preferred polybutene additive, additives such as polyethylene, polypropylene, and polypentene can be employed; moreover, the various isomers of the polyolefins find utility in the invention, as well as diolefins and mixed polymers (e.g., co- and terpolymers). Finally, various types of polyolefin derivatives can also be employed, such as polyolefinic substituted with various moieties such as aryl groups and the like.

In certain forms of the invention, use can also be made of additional additives such as an aromatic compound (e.g., toluene) and another fuel different than the base hydrocarbon (e.g., diesel fuel in the case of a gasoline-based fuel).

In another aspect of the invention, liquid emulsified fuels are provided which broadly include respective quantities of a liquid hydrocarbon combustible fuel, water, at least one surfactant, and an additive selected from the group consisting of polyolefins having recurring C_2-C_{10} monomers therein. Here again, the combustible fuel is advantageously selected from the group consisting of the gasolines, diesel fuels and heavy fuel oils, although other possibilities such as the residual oils could also be employed.

Preferably, the combustible fuel component is present at a level of from about 5 to 99% by weight, and more preferably from about 55 to 90% by weight. On the other hand, the water fraction is preferably present at a level of from about 1 to 95% by weight, and most preferably from about 10 to 45% by weight. In the case of emulsified fuels, the polyolefinic additive should be present at a level of up to about 2.5% by weight, and more preferably at a level of from about 0.1 to 2% by weight.

Various types of surfactants can be employed in the invention, in order to produce stable emulsions having good handling and combustion characteristics. Broadly speaking, one or more surfactants can be used, although in practice it has been found that a combination of surfactants is best suited to the purposes of the invention. The surfactants should be present at a level of up to about 5% by weight, but in this case the prime consideration is one of cost. That is to say, an excess amount of surfactants may not deleteriously affect the characteristics of the fuel, but would be impractical from an economic standpoint.

Brief Description of the Drawing

The single Figure is a plot obtained during the tests described in Example I and illustrates the gain in horsepower/unit of fuel obtained with the improved fuels of the invention, and also that in the case of the indoline hydrocarbon fuel use of polybutene at a level above about 1% by weight is disadvantageous.

Description of the Preferred Embodiments

In the production of non-emulsified fuels in accordance with the invention, the selected polyolefin additive is simply mixed with the hydrocarbon base fuel material at the desired level of addition. The most preferred hydrocarbon bases are the gasolines and diesel fuels (particularly #2 diesel fuel), whereas the poleolefin additive is most preferably polybutene. In the latter connection, the polybutene should be dispersible in the hydrocarbon fuel being used, and advantageously has an average molecular weight of from about 500 to 2,000, and includes recurring isobutane monomers and a terminal olefinic group.

One particular commercially available polybutene used to good effect in the invention is commercialized by the Chevron Chemical Co. as "Polybutene Grade 24." This material is a pale colored, chemically inert oily liquid of moderate to high viscosity and tackiness. The chemical and physical properties of this product are set forth in a publication from the manufacturer entitled "Technical Data Sheet Chevron Polybutenes" dated November 13, 1981. This data sheet is expressly incorporated by reference herein. Briefly, however, the polybutene Grade 24 material has a specific gravity at 15/15° C. of 0.898 (ASTM D 287), a density at 15/15° C. of 7.48 pounds per gallon and an average molecular weight (Mechrolab Osmometer) of 950. The presently most preferred non-emulsified fuel composition consists essentially of about 99.5% of base hydrocarbon fuel, particularly gasoline or #2 diesel oil, along with 0.5% of polybutene admixed therein.

In the context of emulsified fuels, the most preferred fuels include the polybutene Grade 24 additive described above, along with a substantial fraction of water in order to form a water-in-fuel emulsion. Here again, a wide variety of fuels can be employed, but the presently preferred hydrocarbon base fuels include members taken from the group consisting of the gasolines, diesel fuels and heavy fuel oils.

In terms of surfactants, the most preferred combination includes respective minor amounts of three emulsifiers, namely: "TOXIMUL D", an anionic/nonionic blend emulsifier sold by the Stepan Chemical Co. and identified as calcium dodecyl benzene sulfonate/alkyl phenoxy polyoxyethylene ethanol blend, "Ammonyx LO", sold by Onyx Chemical Co. and identified as dodecyldimethyl-amine oxide; and "Atpet-200" sold by ICI Americas and identifed as a sorbitan tallate. In addition however, various other kinds of surfactants can be used to good effect in the invention, such as "Z-MAZ 90" sold by Mazer Chemical Co. and identified as sorbitan monotallate. As those skilled in the art will readily perceive, however, an extremely large number of specific surfactants and combinations thereof can be used in the invention, as long as the aims thereof are achieved. In addition, the preferred emulsifier blend may have applicability in other types of emulsified fuels which do not contain the olefinic additive hereof.

The following table sets forth the constituents of the especially preferred emulsified fuels in accordance with the invention, along with the most preferred levels of use thereof and appropriate ranges:

TABLE 1[1]

Preferred Emulsified Fuel Constituents	Range	Most Preferred
#2 Diesel Oil	65 - 94.15	77.5%
Water	5 - 30	20
Total Emulsifier(s)	0.75 - 3.5	2.0
TOXIMUL D	0.3 - 1.3	0.75
Ammonyx-LO	0.2 - 0.9	0.5
Atpet-200	0.3 - 1.3	0.75
Polyolefin	0.1 - 1.5	0.5

[1] All data in % by weight

In order to produce emulsions in accordance with the invention, it is preferred to first mix the surfactants to be employed, whereupon these surfactants are added to the hydrocarbon base material, with sufficient mixing to ensure homogeneity. At this point, the water is added, again with mixing to assure a relatively even dispersion. The preferred surfactant package described above greatly facilitates the mixing procedure, and no special equipment or the like is required. In the case of gasoline-based emulsions, it is estimated that the average particle diameter of the water in the emulsion is up to about 1/2 micron.

The following examples will illustrate specific fuels in accordance with the invention, as well as salient desirable properties thereof. It is to be understood, however, that these examples are provided for purposes of illustration only.

EXAMPLE I

In order to determine the degree of combustion enhancement using polyolefin-supplemented distillate hydrocarbon fuels having a major proportion of a hydrocarbon base fuel distilling within the gasoline distillation range, engine tests under load simulated by dynamometer were conducted in the laboratories of the University of California at Los Angeles, Los Angeles, California. A Ford, 132-Horsepower (3600 RPM), 6 cylinder engine with a bore of 4.0 inches, a stroke of 3.98 inches, a displacement of 300 cubic inches, compression ratio of 7.9, and torque of 241 ft-lbs. at 1800 RPM was used with a dynamometer equipped with constant speed or constant load modes of automatic control throughout tests. Reference fuel was 91 Octane Indoline test fuel purchased from Amoco Oil Company.

The test program included addition of polybutene (Polybutene grade 24 purchased from the Chevron Chemicals Co. of San Francisco, California) at levels ranging from 0.25% to 2% by weight, to the Indoline test fuel to obtain ratios of work output/fuel consumed at standard engine RPM and torque load levels. Engine RPM was measured and monitored by digital pulse counter from about 700 RPM to maximum of 3,000 RPM. Torque load was held at 52.5 ft-lbs. In one test, a level of 0.3% by weight polybutene was selected for testing at three RPM levels (1,500, 2,000, 2,500) and 52.5 ft-lbs. of torque. As a comparison, straight Indoline was also run at these same RPM and torque levels to give the following results: at 1500 RPM and 52.5 ft-lbs., a work output/pound of straight indoline fuel of 91.5 HP/pound was recorded; at 2000 RPM, 52.5 ft-lbs., 91.1 HP/pound; at 2500 RPM, 52.5 ft-lbs., 89.3 HP/pound. Table II sets forth the results of this test.

As can be seen, in all instances the presence of polybutene increased the work output per pound of fuel, as compared with the straight Indoline test fuel. The percentage increases in combustion enhancement are significant, thereby confirming the value of polyolefin supplementation.

In a second series of tests, polybutene was added to the indoline test fuel at varying

TABLE II

Fuel Composition[1]				Test Conditions			
Indoline	Polybutene	Toluene	Diesel Fuel	RPM	Torque Loss	Work output/pound fuel[2]	Increase in Combustion Enhancement[3]
99.7	0.3	--	--	1,500	52.5 ft-lb	95.6	4.5
99.7	0.3	--	--	2,000	52.5	96.4	5.8
99.7	0.3	--	--	2,500	52.5	94.3	5.6

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1 All data given in % by weight.

2 Data reported as horsepower per pound of fuel.

3 Approximate percentages based upon enhancement as compared with use of straight indoline under identical test conditions.

levels ranging from 0.25 to 2.0% by weight. These additive-supplemented fuels were tested as outlined above to determine work output per pound of fuel. In all instances the engine test was performed at 2,000 RPM and 52.5 ft-lbs. torque.

The results of this series of tests are graphically depicted in the accompanying drawing. As can be seen, the work output per pound of fuel increases rapidly (as compared with the unsupplemented indoline) until an additive level of about 1.0% by weight is reached. Between 1.0 and 1.25% by weight, however, the work output per pound of fuel is dramatically decreased, to a point below the unsupplemented indoline. This was an extremely surprising result, and demonstrates that, at least in connection with the specific indoline test fuel used and at the specified conditions, a relatively critical level of polybutene supplementation is required to achieve optimum results.

EXAMPLE 2

In order to quantitatively confirm the results obtained in Example 1 and to more fully establish the viability of additive-supplemented distillate hydrocarbon fuels having a major proportion of a hydrocarbon base fuel distilling within the gasoline distillation range, consumption tests were conducted at Jarama Race Track in Madrid, Spain. Tests were conducted by, and all drivers certified by, the Real Automobil Club de Espana.

Test A was conducted by driving a 1978 Daimler Jaguar with a six cylinder engine (engine was recently installed new and has less than six months usage) having a bore of 92.07 mm, a stroke of 106 mm, and displacement of 4.2 liters, for a duration of approximately ten liters fuel consumption. The Jaguar was first tested using straight 98 octane gasoline and then compared against additive-supplemented 90 octane gasoline containing 0.5% polybutene. Data is listed in Table III and, in the opinion of the test driver, results obtained with the additive-supplemented fuels were "spectacular."

Test B was conducted by driving a 1982 Datsun, model 280ZX, with an engine having a bore of 3.386 mm, a stroke of 79 mm, and displacement of 2.8 liters, and equipped with 5-speed transmission and electronically controlled fuel injection. The auto was driven at the top speed possible for a duration of approximately ten liters fuel consumption. The Datsun was first tested on standard 98 octane gasoline and then compared against additive-supplemented (0.5% by weight polybutene) 90 octane gasoline. The data is set forth in Table III. It should be noted that both cars will not operate on standard 90 octane gasoline without additive supplementation due to detonation ("knocking" or "pinging").

TABLE III

	98 Octane w/o Additive	90 Octane with Additive	% Change
Test A - 1978 JAGUAR			
Fuel Consumption (liters/km)	0.216	0.178	17.61
Average Speed (km/hour)	61.82	88.90	43.80
Test B - 1982 DATSUN			
Fuel Consumption (liters/km)	0.369	0.335	9.10
Average Speed (km/hour)	95.12	96.35	1.29

Another test involved a qualitative comparison of detonation effects between 98 octane and additive-supplemented (0.5% by weight polybutene) 90 octane gasolines using a new Honda, model VF-1000, 1.0 liter, four cycle test motorcycle at Jarama Race Track in Madrid, Spain. The motorcycle was found to detonate using 98 octane gasoline at high temperatures whereas no detonation occurred at high temperatures with the additive-supplemented, 90 octane gasoline.

EXAMPLE 3

In order to demonstrate the advantages of emulsions of the invention containing water and distillate hydrocarbon fuels having a major proportion of a hydrocarbon base fuel distilling within the diesel fuel distillation range, two engine tests were conducted in the Andalucia

Province of Spain. The comparative tests were conducted using straight GAS-OIL A, a known reference fuel, and alternately an emulsion, produced as outlined above and including 77.5% by weight standard GAS-OIL A, 0.75% by weight Atpet-200, 0.50% by weight Ammonyx-LO, 0.50% by weight Polybutene 24 purchased from Ashland Chemical Company and 20% by weight water. During each test, observations without quantitative measurements were made for soot reduction, ease of hot and cold starting and stopping, along with general running characteristics. In all cases, the emulsions were deemed superior to the straight fuel.

Engine Test 1 measured comparative fuel consumption of straight GAS-OIL A and the emulsified GAS-OIL A during operation of a Diter, D302.1, 16 HP, one cylinder diesel engine with a displacement of 745 cc used to power constant load water pump at 2,300 RPM. Test 2 compared fuel consumption of straight GAS-OIL A and emulsified GAS-OIL A while operating a four cylinder, Mercedes 200D diesel engine. It was evident during Test 2 that the Mercedes produced more power while consuming emulsified GAS-OIL A as opposed to GAS-OIL A without emulsion although the amount was not quantitatively measured. Consumption results are set forth below:

TABLE IV

DIESEL ENGINE FUEL CONSUMPTION COMPARISON

	Gas-oil A	Emulsifed Gas-oil A	% Gain
Test 1	2.33 liter/hr.	1.5 liter/hr.	35.62
[1]Test 1 Corrected		1.2 liter/hr.	48.50
Test 2	4.50 liter/hr.	2.60 liter/hr.	42.22
[1]Test 2 Corrected		2.08 liter/hr.	53.78

[1] Corrected for presence of water in emulsified fuels to give comparable results in terms of amounts of hydrocarbon present in both the straight and emulsified fuels.

EXAMPLE 4

Tests were conducted to determine the general characteristics of emulsified distillate fuels in a conventional fuel handling system such as a boiler or furnace. Factors considered were pumpability, filterability, ignitability and flare stability. Equipment used was a Century Type J1 oil burner assembly with a Sundstrand fuel pump and Marathon Model T2742 motor. The assembly was modified by the addition of a horizontal, 3 foot long, 5 inch diameter pipe equipped with 2 foot long, 8 inch diameter vertical chamber, and a 5 foot long, 5 inch diameter chimney at the outlet end of the horizontal pipe. A 1/2 inch diameter, horizontal water pipe was installed through the vertical chamber to permit water to be introduced through the pipe without direct flame impingement against the water pipe, and to measure water inlet and outlet temperatures.

Various emulsified fuel formulations were tested under identical conditions and compared against the #2 diesel fuel as a reference. Fuel flow was measured on a weight/time basis (simulated load cell) to obtain calorific input, as was water condensate to measure work output. No consideration was given to efficiency, as the objective was determination of the relative enhancement in combustion chemistry.

All emulsified fuel formulations (up to 40% water) performed satisfactorily. There was no evidence of water separation or filter clogging. The emulsions burned well at all pumping pressures where #2 diesel would burn. Atomization appeared good and no corrosion tendencies were noted. The following Table V sets forth the results of these tests wherein: fuel (1) is an emulsion containing 20% by weight water, 0.5% by weight polybutene 24 (Ashland Chemical), 0.75% by weight TOXIMUL D (Stephan Chemical Co.), 0.75% by weight Atpet-200 (I.C.I. Americas), 0.50% Ammoyx-LO (Onyx Chemical Co.) and 77.5% #2 diesel fuel; fuel (2) is an emulsion containing 15% by weight water, 0.5% by weight polybutene, the same emulsifiers and amounts as fuel (1), and 82.5% #2 diesel fuel; fuel (3) is straight #2 diesel fuel; and fuel (4) is identical with fuel (1) except that the polybutene is eliminated and 78% by weight #2 diesel fuel is present.

As can be seen from a comparison of fuels (1) and (4), the presence of polybutene gives a very significant enhancement in work output per pound of fuel. Furthermore, results

TABLE V

Fuel Characteristics	Fuel			
	(1)	(2)	(3)	(4)
Fuel Mass Flow (lbs/hr)	4.789	4.790	4.786	4.800
Hydrocarbon Mass Flow (lbs/hr)	3.711	3.952	4.786	3.840
Water Temperature Differential (°F)[1]	9.0	10.2	9.2	4.5
Condensate Mass Flow (lbs/hr)	31.366	34.423	32.738	32.130
Work Output/Fuel Mass Flow (BTU/pound fuel)	58.9	73.3	62.9	30.1
Work Output/Hydrocarbon Mass Flow (BTU/pound of hydrocarbon from diesel fuel)	76.1	88.8	62.9	37.7

[1] Temperature taken at the inlet and outlet of the 1/2 inch water pipe.

demonstrate that in most instances the emulsified fuels are advantageous over straight #2 diesel fuel.

In addition to the foregoing, limited comparative performance testing was conducted in a small boiler in Kansas City, Missouri. The boiler was a 75 HP Kewanee steam boiler set to 7 1/2 psig high pressure cut-off, 4.0 psig low pressure cut-off. The load consisted of 5 fan driven space heaters (fans approximately 20 inch diameter). Fuel samples contained in drums of 21 5/16 inch diameter were measured volumetrically. Water measurement was accomplished by passing the boiler fill line run through a Signet MK 515 Flosensor with MK575R Flowmeter.

The boiler was brought up to pressure on minimum fire with the fuel bypass modulator valve locked in the minimum position. Approximately six minutes after high pressure shut down, the boiler was filled with water until the pump was shut off by the high level switch. The water flowmeter was then reset to zero and the fuel level measured. The boiler was allowed to fire automatically by the high and low steam pressure switches through four complete cycles. At approximately six minutes after high pressure shut down on the fourth firing cycle, the boiler was again filled and final measurements taken of the fuel level and water meter reading.

CO_2 increased from 11%, firing #2 diesel fuel (reference fuel), to 12.5%, firing emulsified diesel fuel (same as fuel (1), Table IV) indicating increased combustion efficiency. The fire became unstable when switched to emulsified fuel because, according to the Testing Engineer, there was insufficient excess air (oxygen) to support combustion. Excess air was opened to approximately maximum (supporting more than 3MM BTU/hour combustion), and fuel flow rate was reduced to minimum (approximately 1.2MM BTU/hour) and there was still insufficient air to support combustion. This indicates that the emulsified fuel of the invention had a combustion efficiency greatly in excess of straight #2 diesel fuel.

EXAMPLE 5

Various tests were conducted and certified under the direction of the Ministerio de Defensa at the Instituto Nacional de Tecnica Aeroespacial in Madrid, Spain. Results were recorded in certification number 40180 as follows with respect to 4 emulsions produced in accordance with the present invention:

Emulsion #1 - 20% by weight water, 0.5% by weight polybutene, 2.0% by weight emulsifiers (0.75% by weight T-MULZ-D, 0.75% by weight Atpet-200 and 0.5% by weight Ammonyx-LO) and 77.5% by weight GAS-OIL A -
pH - 7.8
Viscosity at 37.8°C - 6.2 cSt (centistokes)
Filtration - Passes unencumbered
Stability - Stable

Emulsion #2 - 20% by weight water, 0.5% by weight polybutene, 2.0% by weight emulsification agents (same makeup as Emulsion #1) and 77.5% by wegiht GAS-OIL B -
pH - 7.5

Viscosity at 37.8°C - 5.4 cSt
Filtration - Passes unencumbered
Stability - Stable

Emulsion #3 - 20% by weight water, 0.5% by weight polybutene, 2.0% by weight emulsification agents (same makeup as Emulsion # 1) and 77.5% by weight GAS-OIL C -
pH - 7.7
Viscosity at 37.8°C - 5.7 cSt
Filtration - Passes unencumbered
Stability - Stable

Emulsion #4 - 20% by weight water, 0.5% by weight polybutene, 2.0% by weight emulsification agents (same makeup as Emulsion #1) and 77.5% by weight residual fuel oil -
Viscosity at 37.8°C - 580.4 cSt
Viscosity at 50.0°C - 331E

These emulsions were stable and remained so over more than two months shelf life.

EXAMPLE 6

In order to determine the ability of emulsified distillate fuels in accordance with the invention to pass through a coalescing filter without separation of water, various emulsified distillate fuel formulations were pumped through a Caterpillar #6M7617 water separator element. Emulsions were pumped by air pressure at 5 psig through the coalescing filter which was mounted in a glass bowl. No free water has been observed in more than five months of testing.

A qualitative comparison of the quantity of sulphur in combustion gases of emulsified and non-emulsified fuel oils was made by sequentially burning various grades of fuel oils in a dish. A 5 inch diameter tube, 1 1/2 foot long was placed over the flame to act as flue stock. Porous filter papers soaked with potassium permanganate solution were placed over the tube for one minute. A bleaching of these papers would indicate the presence of sulphur in the combustion gases.

Both distillate and residual fuel oil samples burned showed marked color change (bleaching). Emulsified residual fuel oil samples not incorporating polyolefins or emulsifiers showed similar color change to the non-emulsified samples of the same fuels although somewhat darker. Fuel oil samples emulsified with water and the preferred emulsifiers and supplemented with polybutene showed no color change when using distillate fuel (#2 diesel) and only a slight color change with residual fuels (#5 and #6).

While the inventors do not wish to be bound to any specific theory as to why the polyolefinic additives of the invention give such outstanding results, it is hypothesized that such additives in some way initiate or promote reactions analogous to cracking during the combustion of the polyolefin supplemented fuel compositions hereof. Under this line of reasoning, such reactions would produce smaller, lower molecular weight hydrocarbons, which are known to be more readily combustible. Moreover, the exothermic heats of reaction would theoretically add substantially to the caloric value obtained from the fuels.

While the foregoing disclosure has been primarily directed to the use of liquid hydrocarbon base materials, it is also believed that the combustibility of solid hydrocarbon material such as coal can be enhanced through the use of polyolefinic agents of the invention. In such a context, the polyolefinic material could be simply sprayed upon crushed coal in order to give enhanced combustion characteristics or, alternatively, the polyolefinic agents could be added to coal/liquid suspensions.

Claims

1. An improved engine fuel essentially free of lubricating oil and comprising a combustible hydrocarbon material, and from about 0.1 to 2.5% byt weight of an additive, the type and amount of said additive serving to increase the work output per unit of fuel obtained using said improved fuel, as compared with the work output per unit of fuel obtained under the same conditions using a fuel identical with said improved fuel except for the absence of said additive, said additive comprising a polyolefinic substance having recurring C_2-Cl_0 monomers therein.

2. The improved fuel of Calim 1, said improved fuel consisting essentially of said hydrocarbon material and said additive.

3. The improved fuel of Claim 1, said material being selected from the group consisting of liquid hydrocarbons.

4. The improved fuel of Claim 3, said liquid hydrocarbons being selected from the group consisting of the gasolines, diesel fuels and heavy fuel oils.

5. The improved fuel of Claim 1, said additive being present at a level of from about 0.1 to 2% by weight.

6. The improved fuel of Claim 5, said level being from about 0.3 to 0.8% by weight.

7. The improved fuel of Claim 1, said additive being selected from the group consisting of polyolefins having recurring C_3-C_6 monomers therein.

8. The improved fuel of Claim 6, said additive being polybutene.

9. The improved fuel of Claim 1, including a minor amount of an aromatic compound admixed withs aid fuel.

10. The improved fuel of Claim 1, including a minor amount of another fuel different than said combustible hydrocarbon material.

11. An improved four-cycle engine fule essentially free to lubricating oil and comprising gasoline and from about 0.1 to 1% by weight of polybutene.

12. The improved fuel of Claim 11, said engine fuel consisting essentially of gasoline and polybutene.

13. An improved liquid emulsified fuel comprising respective quantities of a liquiid hydrocarbon combustible fuel, water, at least one surfactant, and an additive selected from the group consisting of polyolefins having recurring C_2-C_{10} monomers therein.

14. The emulsified fuel of Claim 13, said combustible fuel being selected from the group consisting of the gasolines, diesel fuels and heavy fuel oils.

15. The emulsified fuel of Claim 13, said combustible fuel being present at a level of from about 5 to 99% by weight.

16. The emulsified fuel of Claim 13, said water being present at a level of from about 1 to 90% by weight.

17. The emulsified fuel of Claim 13, said additive being present at a level of up to about 2.5% by weight.

18. The emulsified fuel of Claim 17, said level being from about 0.1 to 2% by weight.

19. The emulsified fuel of Claim 13, said surfactant being present at a level of up to about 5% by weight.

20. The emulsified fuel of Claim 13, including a plurality of surfactants.

21. An emulsified fuel comprising respective quantities of a liquid hydrocarbon combustible fuel, water, and a surfactant system comprising (1) alkaline earth dodecyl benzene sulfonate/alkyl phenoxy polyoxyethylene ethanol blend; (2) dodecyldimethylamine oxide; and (3) sorbitan tallate.

AMENDED CLAIMS

[received by the International Bureau on 30 October 1985 (30.10.85);
original claims 1,3- 7,9,10,14-17 cancelled; claims 2,11,12,13,18 and 21 amended;
new claims 22-24 added (3 pages)]

1. (Cancelled)

2. The improved fuel of Claim 22, said improved fuel consisting essentially of said hydrocarbon material and said additive.

3. (Cancelled)

4. (Cancelled)

5. (Cancelled)

6. (Cancelled)

7. (Cancelled)

8. The improved fuel of Claim 22, said additive being polybutene.

9. (Cancelled)

10. (Cancelled)

11. A four-cycel engine fuel essentially free of lubricating oil and comprising gasoline and from about 0.3 to 0.8% by weight of polybutene.

12. The fuel of Claim 11, said engine fuel consisting essentially of gasoline and polybutene.

13. A liquid emulsified fuel comprising from about 5 to 99% by weight hydrocarbon combustible fuel selected from the group consisting of the gasolines, diesel fuels and heavy fuel oils, from about 1 to 90% by weight water, at least one surfactant for giving a stable emulsion with the fuel and water, and up to about 2.5% by weight of an additive selected from the group consisting of polyolefins having recurring C_2-C_{10} monomers therein.

14. (Cancelled)

15. (Cancelled)

16. (Cancelled)

17. (Cancelled)

18. The emulsified fuel of Claim 13, said level being from about 0.1 to 2% by weight.

19. The emulsified fuel of Claim 13, said surfactant being present at a level of up to about 5% by weight.

20. The emulsified fuel of Claim 13, including a plurality of surfactants.

21. An emulsified fuel comprising respective quantities of a liquid petroleum combustible fuel, water, and up to about 5% by weight of a surfactant system comprising (1) alkaline earth dodecyl benzene sulfonate/alkyl phenoxy polyoxyethylene ethanol blend; (2) dodecyldimethylamine oxide; and (3) sorbitan tallate.

22. A liquid engine fuel essentially free of lubricating oil and comprising a combustible liquid hydrocarbon material selected from the group consisting of the gasolines, diesel fuels and heavy fuel oils, from about 0.3 to 0.8% by weight of an additive comprising a polyolefinic substance having recurring C_3-C_6 monomers therein, said substance having a relatively low molecular weight such that the substance is in the form of a liquid at normal ambient conditions.

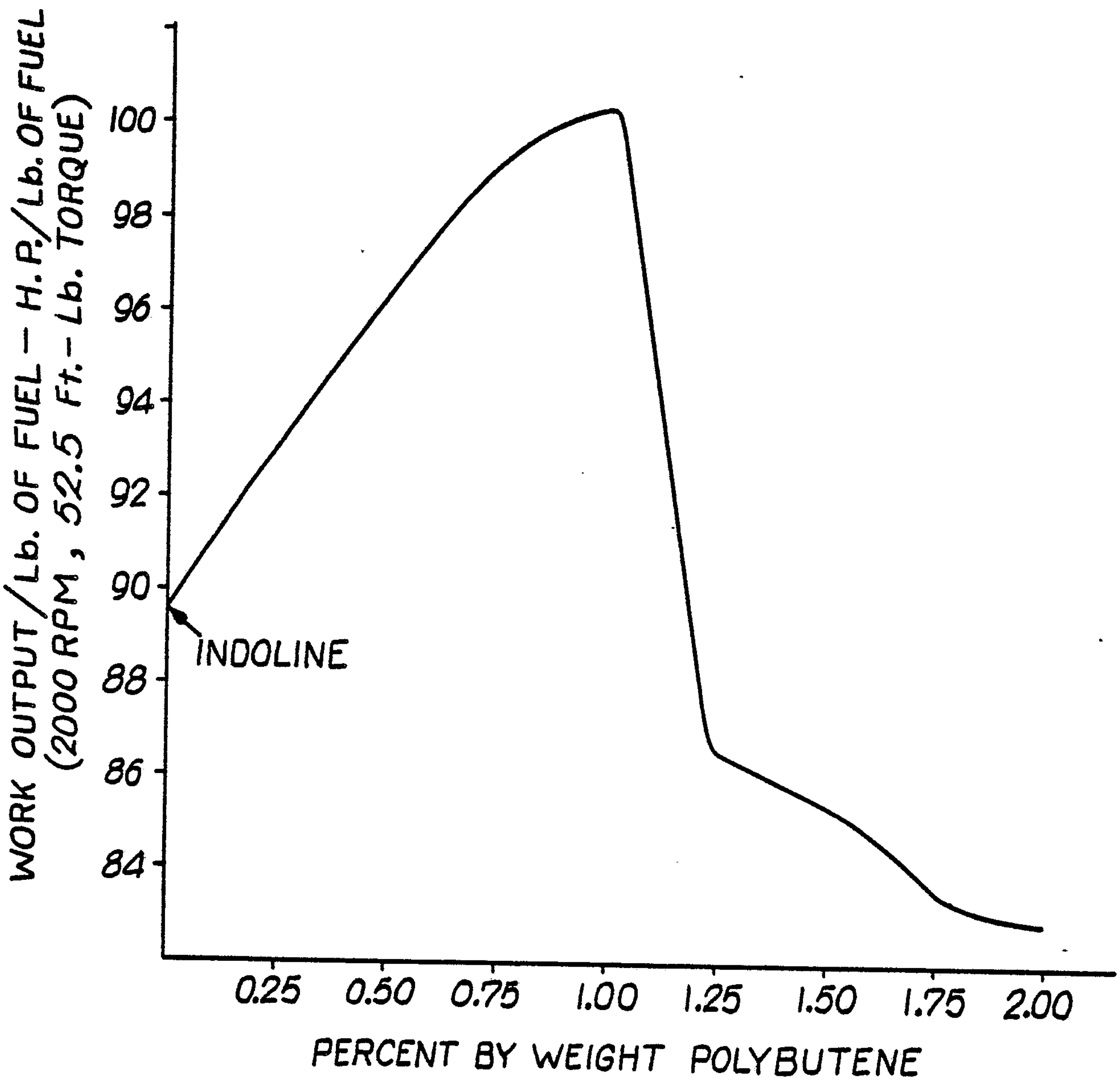
23. The emulsifed fuel of Claim 13, said additive being selected from the group consisting of polyolefins having recurring C_3-C_6 monomers therein.

24. The emulsified fuel of Claim 23, said additive being polybutene.

STATEMENT UNDER ARTICLE 19

Claims 22, 2, 8, 11 and 12 relate to fuel compositions which are essentially free of lubricating oil and comprise a combustible material and from about 0.3 - 0.8% by weight of a polyolefinic additive such as polybutene therein. Claim 22 is a replacement for original Claim 1.

Claims 13, 18-20 and 23-24 all define emulsified fuels in accordance with the invention which comprise specific quantities of combustible fuel, water, surfactant and polyolefinic additive. Claim 21 has been amended to more particularly recite the preferred surfactant composition used in emulsified fuel compositions.


WORK OUTPUT/Lb. OF FUEL - H.P./Lb. OF FUEL
(2000 RPM, 52.5 Ft.-Lb. TORQUE)
100
98
96
94
92
90
88
86
84
INDOLINE
0.25
0.50
0.75
1.00
1.25
1.50
1.75
2.00
PERCENT BY WEIGHT POLYBUTENE

INTERNATIONAL SEARCH REPORT

International Application No PCT/US85/01209

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) [3]

According to International Patent Classification (IPC) or to both National Classification and IPC

INT Cl[4] C10L 1/18
US Cl 44/57

II. FIELDS SEARCHED

Minimum Documentation Searched [4]

Classification System	Classification Symbols
U.S.	44/57, 62, 51

Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched [5]

III. DOCUMENTS CONSIDERED TO BE RELEVANT [14]

Category *	Citation of Document, [16] with indication, where appropriate, of the relevant passages [17]	Relevant to Claim No. [18]
X	US, A, 4,381,414 (BEACH ET AL), 26 APRIL 1983	1-8 and 12
X	US, A, 3,996,023 (OSMOND ET AL), 12 DECEMBER 1976	1-8 and 12
X	US, A, 3,838,990 (MIEVILLE), 1 OCTOBER 1974	1-8 and 12
X	US, A, 3,502,451 (MOORE ET AL), 24 MARCH 1970	1-8 and 12
X	US, A, 3,488,704 (LOVETT ET AL), 6 JANUARY 1970	1-8 and 12
X	US, A, 3,454,379 (ISAACSON ET AL), 8 JULY 1969	1-7
X	US, A, 4,175,926 (WISOTSKY), 27 NOVEMBER 1979	1-7
Y	US, A, 2,550,982 (EBERTZ), 1 MAY 1951	21

* Special categories of cited documents: [15]

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"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

"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

IV. CERTIFICATION

Date of the Actual Completion of the International Search [2]	Date of Mailing of this International Search Report [2]
6 SEPTEMBER 1985	16 SEP 1985
International Searching Authority [1]	**Signature of Authorized Officer [20]**
ISA/US	MRS. Y. HARRIS-SMITH

Form PCT/ISA/210 (second sheet) (October 1981)

FURTHER INFORMATION CONTINUED FROM THE SECOND SHEET

Y	US, A, 2,873,182 (KOSMIN), 10 FEBRUARY 1959	21
Y	US, A, 4,477,258 (LEPAIN), 16 OCTOBER 1984	21

V.☐ OBSERVATIONS WHERE CERTAIN CLAIMS WERE FOUND UNSEARCHABLE [10]

This international search report has not been established in respect of certain claims under Article 17(2) (a) for the following reasons:

1.☐ Claim numbers ...., because they relate to subject matter [12] not required to be searched by this Authority, namely:

2.☐ Claim numbers ...., because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out [13], specifically:

VI.☐ OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING [11]

This International Searching Authority found multiple inventions in this international application as follows:

1.☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims of the international application.

2.☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims of the international application for which fees were paid, specifically claims:

3.☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claim numbers:

4.☐ As all searchable claims could be searched without effort justifying an additional fee, the International Searching Authority did not invite payment of any additional fee.

Remark on Protest

☐ The additional search fees were accompanied by applicant's protest.

☐ No protest accompanied the payment of additional search fees.