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METHOD OF MAKING JET FUEL AND USE THEREOF

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This invention relates to a method of making a jet fuel. In another aspect it relates to the use of such fuel in a jet engine.

It has been proposed to produce jet fuels by hydrogenating a mixture of unsaturated polycyclic hydrocarbons. When conducted without a preliminary hydrodesulfurization step, the product contains some unsaturated materials together with the saturated materials. Fuels produced in this manner range from about 85 percent to about 93 percent saturated. While these fuels yield certain advantages over aliphatic hydrocarbon turbojet fuels, actual tests have demonstrated that considerable difficulties are present when such fuels are utilized. In particular, coke deposits occur in the combustor chamber, the afterburner, and the tail pipe, and particularly at the combustor nozzle. The skin temperature at localized regions within the combustion chamber may become undesirably or even dangerously high. An important contribution to such excessive temperatures is made by undesirable luminosity of the flame from the fuel combustion. Such luminosity causes radiation of heat to the metal and other parts of the engine.

In accordance with this invention, a hydrodesulfurized highly aromatic feedstock is hydrogenated to provide a fuel which is 95 to 100 percent saturated. This fuel is utilized in a jet engine with the result that undesirable coke deposits are substantially or completely eliminated, and the luminosity of the flame is reduced to acceptable levels, thereby preventing the occurrence of undesirable hot spots in the combustor. Surprisingly, these advantages result in a substantial improvement in performance despite the fact that the hydrogenation reduces the volumetric heat content of the fuel, i.e., its density, a result considered highly undesirable by previous workers.

Where heavy cycle oil is used as a feedstock, a saturation of 95 percent or higher cannot be attained without virtually complete removal of sulfur prior to the hydrogenation step.

The hydrodesulfurization can advantageously be accomplished with the aid of a cobalt molybdate catalyst or, under high hydrogen pressure and elevated temperatures, by treatment with a stoichiometric quantity of sodium.

After the hydrodesulfurization treatment, the highly aromatic stock can be readily hydrogenated until it is 95 percent or more saturated.

In the operation of turbojet engines with the present fuel, air is fed through an air compressor to the combustion chamber of the engine, which is formed from refractory metals or alloys designated to withstand specific combustion temperatures. In this chamber, the fuel and air are mixed, and the mixture is ignited.

The resulting burned mixture is diluted with secondary air in an afterburner and expanded through a turbine which drives an air compressor. Thereupon, the gases are ejected through a jet or tail pipe into the atmosphere with resulting production of a forward thrust. In turboprop engines, the principle of operation is essentially the same except that the majority of the energy is expended in driving the turbine which, in turn, is connected to a propeller.

Due to the large number of intricately shaped vanes in the turbine, it is evident that coke deposits are a very serious problem, as are such deposits in the combustion chamber or nozzle. Moreover, if the design temperature

at localized regions within the engine is exceeded, it is evident that serious damage to the engine can result, or even a catastrophic failure.

The feedstocks utilized in the process of this invention are aromatic fractions built up during the catalytic cracking of gas oil. They are derived by extraction, usually with sulfur dioxide or furfural, of catalytic cracker cycle oil. The aromatic extract boils within the range of 450 to 1,000° F. at atmospheric pressure. It is characterized by a sulfur content of 0.25 to 2.5 weight percent, a nitrogen content of .03 to .3 weight percent and an oxygen content of 0.25 to 2.5 weight percent. The oil is at least 50 volume percent aromatic as determined by silica gel absorption, the aromatic components being polynuclear polyalkylated aromatics.

To obtain the maximum advantages of the invention, it is desirable to increase the volume percent of aromatic material to at least 95 percent prior to the hydrodesulfurization step. This can be effected by an additional extraction step, for example, with solvents such as dimethylsulfoxide.

The aromatic oil is then hydrodesulfurized. This can be effected by treatment with catalysts such as cobalt molybdate, molybdenum oxide, molybdenum sulfide, tungsten sulfide or other known hydrodesulfurization catalysts. As those skilled in the art will understand, the hydrodesulfurization is effective to remove oxygen and nitrogen-containing compounds as well as the sulfur compounds. In one aspect of the invention, the sulfur is removed by treatment with a stoichiometric quantity of sodium (based on sodium sulfide formation) under high hydrogen pressure and elevated temperatures. The quantity of hydrogen utilized in the hydrodesulfurization must be at least the stoichiometric equivalent of the quantity of sulfur, nitrogen, and oxygen present in the feed to the hydrodesulfurization step plus the quantity required to replace the sulfur, nitrogen and oxygen. To insure complete removal of these materials, the hydrogen should be at least 150 percent of the theoretical quantity required.

In order that the fuel may have a final saturation of at least 95 percent in accordance with the invention, it is essential that virtually complete removal of the sulfur, nitrogen and oxygen compounds be effected. In particular, the sulfur content of the hydrodesulfurized material should be less than 0.05 percent, the nitrogen content should be below 0.05 percent, and the oxygen content should be below 0.1 percent.

The conditions of temperature and pressure for the hydrodesulfurization step are well known to those skilled in the art and form no part of this invention. Suitable conditions are a total pressure of 1,000 pounds per square inch and a temperature of 750° F.

The material is then hydrogenated to provide a fuel which is 95 to 100 percent saturated. To this end, catalytic hydrogenation with a nickel, platinum or other known hydrogenation catalyst is suitable. Suitable hydrogenation conditions are well known to those skilled in the art. In general, the amount of hydrogen utilized ranges from 2500 to 5000 cubic feet per barrel hydrogenated. A pressure of at least 1,000 pounds per square inch or higher is suitable, and temperatures may range from 400 to 600° F.

When the hydrogenated material is used as fuel in a jet engine in the manner hereinbefore described, coking in the combustion chamber and other parts of the engine is minimized or wholly eliminated, and the presence of localized hot spots in the combustion chamber with resulting serious damage to the engine is eliminated. We attribute this to the fact that our fuel is at least 95 percent saturated, and has a luminometer reading of at least 30. The luminosity of the fuel is determined by burning it in a small wick-type lamp which is provided with an optical

filter and photocell circuit sensitized to the range of 4,800 to 7,000 angstrom units. A dual thermocouple circuit and potentiometer directly indicates the lamp temperature rise. The luminosity is determined according to the following formula by comparing the temperature rise across the burner to that obtained with the reference fuels, tetralin and isooctane.

$$\text{Luminosity}=\frac{\Delta T \text{ Test Fuel}-\Delta T \text{ Tetralin}\times 100}{\Delta T \text{ Isooctane}-\Delta T \text{ Tetralin}}$$

This is not a linear measurement, and luminometer readings of less than 30 have been found to give rise to unsatisfactory operating conditions, particularly the production of localized hot spots, in the operation of jet engines. It is surprising that the fuel of this invention realizes the foregoing advantages and yet maintains a high net heat of combustion in excess of 130,000 B.t.u. per gallon, the heat of vaporization of the water of combustion being excluded from this figure. Moreover, the jet fuels of the invention have low pour points below −10° F., for example, −35° F. The density ranges between 0.850 and 1.000 gram per cubic centimeter measured at 20° C.

It is a feature of the invention that a practically quantitative removal of unsaturation can be effected by treating the hydrogenated material with silica gel. This results in even greater advantages, particularly as regards coke disposition and production of hot spots. In particular, by this final treatment, materials having a saturation of 99.5 percent or more can be obtained. Instead of utilizing silica gel, the final treatment may be effected by treatment with sulfuric acid and water-washing the thus treated material.

SPECIFIC EXAMPLE

In one specific run, the novel jet fuel composition of the invention was made from a sulfur dioxide extract of a cycle oil from a catalytic cracking operation. The oil had the following characteristics.

Sulfur	1.6 weight percent.
Refractive index (20° C.)	1.5900.
Density, grams per cc	0.995.
Atomic ratio of carbon to hydrogen	0.812.
Weight percent nitrogen (Dumas Method)	0.16.
Pour point	35° F.
Aniline point	66.8° F.
Carbon residue	2.53 weight percent.
Bureau of Mines correlation index	92.
Volume percent non-aromatic material	24.8.

Two percent of the material was distilled at 518° F. and 95 percent of the material was distilled at 890° F. at atmospheric pressure.

This oil was solvent extracted with dimethylsulfoxide at 180° F. and a solvent/oil ratio of 3/1. The extract yield was about 75 volume percent of the charge and had a gravity of 2.7 API (density of 1.054 g./cc.). The extract was about 5 volume percent non-aromatics.

The extract from the preceding step was treated by passing it twice over a cobalt molybdate catalyst which was supported on alumina. The composition corresponded to 3 percent cobalt oxide and 7.5 percent molybdenum oxide. The treatment took place at a pressure of 500 pounds per square inch, a temperature of 800° F., and a liquid hourly space velocity of 1, the amount of hydrogen supplied being 1,000 cubic feet per barrel of feed. After this treatment, a small amount of material boiling at less than 400° F. was separated by fractional distillation from the remainder of the product.

Upon analysis of the product after the described hydrodesulfurization treatment, the amount of sulfur, oxygen and nitrogen present was too high to attain the desired extent of hydrogenation. Accordingly, the material was subjected to another hydrodesulfurization treatment utilizing a cobalt molybdate catalyst supported on alumina, the composition of which corresponded to 4.2% cobalt oxide and 6.6 percent molybdenum trioxide. The conditions used in this step were a temperature of 775° F., and a liquid hourly space velocity of 0.5, the amount of hydrogen supplied being 4,000 cubic feet per barrel of feed. The total treatment time was 6 hours. After this treatment, the sulfur content was 0.05%, and the amount of oxygen and nitrogen originally present had been correspondingly reduced.

The product from the aforementioned hydrodesulfurization steps was fractionated, and 4.9 weight percent of the material, which had a boiling point of less than 400° F., was separated from the rest of the product. About 320 parts of the material boiling above 400° F. was placed in a rocking autoclave and 74 parts of a reduced nickel on kieselguhr hydrogenation catalyst was added. Hydrogen was added periodically at a temperature of 500° F. until no further addition of hydrogen took place at a total pressure of 1500 pounds. The hydrogenated product had a density of 0.909 gram per cubic centimeter at 20° C., a carbon to hydrogen ratio of 87.2:13.0, a refractive index of 1.4907 at 21° C., and a viscosity of 50.56 centistokes at 100° F. or 33.00 at 210° F. The product had a gross heat of combustion of 148,000 B.t.u. per gallon which corresponds approximately to a net value of about 140,000. The pour point was −35° F. The hydrogen consumption during the hydrogenation step was 3270 cubic feet per barrel. The material was 99 percent saturated. A portion of this material was freed of residual aromatics by absorption on silica gel. The eluate was fractionally distilled and separated into fractions as follows:

Fraction	Boiling Point	Volume Percent
1	Less than 400° F.	4.5
2	400 to 500° F.	13.8
3	500 to 600° F.	40.6
4	Over 600° F.	41.1
FRACTIONS DISTILLED FROM FRACTION 4		
5	600 to 700° F.	28.8
6	Over 700° F.	12.3

Fraction 3 had a net heat of combustion of 137,000 B.t.u. per gallon, a molecular weight of 213 determined by the freezing point depression method in benzene, a density of 0.9037 gram per cubic centimeter at 20° C., a viscosity of 5.5 centistokes at 100° C., and a viscosity of 1.70 centistokes at 210° C.

Fraction 4 had an atomic ratio of carbon to hydrogen of 88.3:12.0, a net heat of combustion of 18,247 B.t.u. per pound, a molecular weight of 263 determined by the freezing point depression method in benzene, a density of 0.9367 gram per cubic centimeter at 20° C., a viscosity of 43 centistokes at 210° C., and a luminometer reading of 38.5.

Fraction 5 had a density of 0.9297 gram per cubic centimeter at 20° C. Fraction 6 had a density of 0.9683 gram per cubic centimeter at 20° C. and a net heat of combustion of 145,200 B.t.u. per gallon.

When tested as a jet fuel, after a long period of operation with fraction 3, the engine is much freer from carbon deposits than is the case wherein the engine is operated with a hydrogenated aromatic fraction which is 92–93 percent saturated. Due to the improved degree of luminosity, occurrence of hot spots in the combustion chamber is substantially diminished. The fuel exhibits excellent thermal stability, and the filters do not become clogged with carbon deposits.

While the invention has been described in connection

with a preferred embodiment thereof, it is understood that variations in materials and conditions may be made without departing from the spirit and scope of the invention.

We claim:

1. The method of making a jet fuel, which comprises extracting cycle oil from a catalytic cracking operation with sulfur dioxide, extracting a resulting aromatic fraction extract with dimethylsulfoxide, hydrodesulfurizing the resulting aromatic fraction extract having a sulfur content of 0.25 to 2.5 weight percent in the presence of cobalt molybdate to reduce said sulfur content to less than 0.05 weight percent, and hydrogenating the resulting material until it is 95 to 100 weight percent saturated.

2. The method of making a jet fuel, which comprises extracting cycle oil from a catalytic cracking operation with a solvent selected from the group consisting of sulfur dioxide and furfural, extracting the resulting aromatic fraction extract with dimethylsulfoxide, the resulting aromatic fraction extract boiling within the range of 450 to 1000° F. at atmospheric pressure and having a sulfur content of 0.25 to 2.5 weight percent, hydrodesulfurizing the latter aromatic fraction extract with hydrogen in the presence of a hydrodesulfurizing catalyst selected from the group consisting of cobalt molybdate, molybdenum oxide, molybdenum sulfide, and tungsten sulfide to reduce the sulfur content to less than 0.05 weight percent, the nitrogen content to below 0.25 weight percent and the oxygen content to below 0.1 weight percent, and hydrogenating the resulting material in the presence of a hydrogenation catalyst to provide a fuel which is 95 to 100 weight percent saturated and has a luminometer of at least 30.

3. The method of making a jet fuel, which comprises extracting cycle oil from a catalytic cracking operation with sulfur dioxide, extracting the resulting aromatic fraction extract with dimethylsulfoxide to provide an aromatic fraction extract boiling within the range of 450 to 1000° F. at atmospheric pressure and having a sulfur content of 0.25 to 2.5 weight percent, a nitrogen content of 0.03 to 0.3 weight percent and an oxygen content of 0.25 to 2.5 weight percent, hydrodesulfurizing the latter aromatic fraction extract with hydrogen in the presence of cobalt molybdate to reduce the sulfur content to less than 0.05 weight percent, the nitrogen content to below 0.05 weight percent and the oxygen content to below 0.1 weight percent, hydrogenating the resulting material in the presence of a catalyst comprising nickel to provide a hydrogenated product which is 95 to 100 weight percent saturated and has a luminometer value of at least 30, treating the said hydrogenated product with a compound capable of absorbing aromatic material to provide a material which is 99 to 100 weight percent saturated, and fractionating the thus treated material to provide a fuel having a preselected boiling range for jet engine operation.

4. The method of operating a jet engine, which comprises mixing fuel and air in a combustion chamber, causing combustion of said fuel and air, and ejecting the combustion gases through a nozzle to produce a propulsive thrust, said fuel being prepared by extracting cycle oil from a catalytic cracking operation with a solvent selected from the group consisting of sulfur dioxide and furfural, extracting the resulting aromatic fraction extract with dimethylsulfoxide, the resulting aromatic fraction extract boiling within the range of 450 to 1000° F. at atmospheric pressure and having a sulfur content of 0.25 to 2.5 weight percent, a nitrogen content of 0.03 to 0.3 weight percent, and an oxygen content of 0.25 to 2.5 weight percent, hydrodesulfurizing the latter aromatic fraction extract with hydrogen in the presence of a hydrodesulfurizing catalyst selected from the group consisting of cobalt molybdate, molybdenum oxide, molybdenum sulfide, and tungsten sulfide to reduce the sulfur content to less than 0.05 weight percent, the nitrogen content to below 0.05 weight percent and the oxygen content to below 0.1 weight percent, and hydrogenating the resulting material in the presence of a hydrogenation catalyst to provide a fuel which is 95 to 100 weight percent saturated and has a luminometer of at least 30.

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