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TREATMENT OF HYDROCARBONS

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This invention relates to the treatment of hydrocarbons. More particularly it relates to the production of improved fuels for gas turbine engines.

Fuels currently in use for the propulsion of "jet aircraft," as gas turbine powered aircraft are commonly called, are kerosene, JP–4 and JP–5, the last two being military specifications (MIL–F–5624C amend. 1). While these fuels are satisfactory to the extent that they perform the desired functions there are several disadvantages attached to their use in gas turbine powered aircraft.

One of the disadvantages of the fuels currently in use is that they produce excessive smoke during take-off. To eliminate this problem it is customary to inject a mixture of water and alcohol into the engine with the fuel during take-off. While this technique presents a solution to the problem of excessive smoke it necessitates a dual tankage system in the aircraft and also includes another complication at a critical moment in the operation of the aircraft.

Another disadvantage attached to the use of current jet engine fuels is the necessity of frequent engine overhauls. In the operation of a gas turbine engine, atmospheric air is compressed and is then introduced into the combustion section where it is heated by burning fuel therein. The hot gases are then expanded through a turbine and exhausted to the atmosphere through a jet or tailpipe. The combustion takes place in a combustion chamber into which a portion of the compressed air, sometimes called primary air, is mixed with a fuel spray in approximately the stoichiometric ratio to support combustion and the balance of the air, sometimes called secondary air, is introduced into the hot combustion gases to cool them to a temperature which can be tolerated by the downstream parts including the turbine inlet nozzles and blading. The combustion zone is surrounded by a metallic liner or flame tube. The liner is subjected to considerable thermal stress and generally when the fuels currenily in use are employed in the gas turbine engine the liner, which surrounds a flame of 3000° F. or higher, is subjected to extreme stress principally due to radiation from the flame, which results in creeping, warping and buckling of the part. In some instances the high radiation from the flame also causes buckling of the turbine rotor to such an extent that malfunctioning and sometimes complete failure of the engine results. For this reason, it is customary to inspect the gas turbine engines frequently and experience has shown that a fairly thorough overhaul is necessary after about 500–600 hours of operation.

Prior to the present invention it was believed that high thrust could be obtained using fuels having a relatively high B.t.u. per gallon ratio. It has now been found, to the contrary, that the operation of gas turbine aircraft is considerably improved when the fuel has a high B.t.u. per pound ratio.

In copending application Serial No. 778,607, filed December 8, 1958, it is disclosed that fuels having a luminosity number of at least 100 and preferably 125 and having a high B.t.u. per pound ratio are considerably superior to fuels having a high B.t.u. per gallon ratio and a luminosity number of less than 100. These fuels, that is, fuels having a luminosity number of at least 100 and preferably at least 125, eliminate the necessity of dual tankage in aircraft as they do not produce excessive smoke

during take-off. It is also disclosed that when gas turbine engines using fuels having a luminosity number of at least 100 and preferably at least 125 are used, the necessity for complete inspection and overhaul of the engine is reduced to a frequency of not oftener than about every 1000 hours of operation.

It has been found that when the fuel is not only low in aromatics but is also low in the naphthenes and consequently has a high luminosity number and burns with a flame of low radiation, gas turbine engines can be operated at an increased thrust level without increasing the frequency of overhaul.

It is an object of the present invention to produce improved fuels suitable for use in gas turbine engines. Another object of the invention is to produce a gas turbine engine fuel having a luminosity number of at least 100. Another object of the invention is to produce a fuel having low aromatic and naphthene content. These and other objects will be obvious to those skilled in the art from the following disclosure.

According to the invention a hydrocarbon liquid such as naphtha, e.g. straight run naphtha, cracked naphtha, coker naphtha, or mixtures thereof or materials boiling in the kerosene range or mixtures of naphtha and kerosene are contacted with an isomerization catalyst to convert at least a portion of the alkyl C_5 ring naphthenes to C_6 ring naphthenes. A particularly suitable isomerization catalyst is a platinum on alumina catalyst having a high halogen content, specifically at least 3% by weight fluorine. When the high fluorine platinum isomerization catalyst is used, the isomerization may be carried out at a temperature of from about 600 to 800° F., a pressure of 50 to 700 p.s.i.g., a liquid hourly space velocity of 0.5–5 v./v./hr. and a hydrogen to hydrocarbon mol ratio of from 1:1–10:1. Preferred conditions are temperatures of about 650 to 750° F., pressures of about 100 to 500 p.s.i.g., a hydrogen to hydrocarbon mol ratio of about 4:1 and space velocities of from 1 to 3.

The isomerization product is then contacted with a dehydrogenation catalyst to convert the C_6 ring naphthenes to aromatics. Suitable dehydrogenation catalysts are platinum on alumina optionally containing combined halogen, molybdenum oxide on alumina or chromium oxide on alumina. The dehydrogenation of the naphthenes using a molybdenum oxide on alumina catalyst containing 9–10% molybdena may be effected at a temperature of about 900 to 1000° F., a pressure ranging from 50 to 500 p.s.i.g. and a space velocity of about 0.5–3 volume of feed per volume of catalyst per hour. When a chromia alumina catalyst containing from about 12–20% chromia is used, preferred operating conditions are 900–1000° F., 0–500 p.s.i.g., and a space velocity of about 0.5–3 v./v./hr. For the platinum catalyst, which should be essentially free from acid materials such as halogen or silica to minimize reverse isomerization and to reduce cracking and the resulting deactivation of the catalyst due to the deposition of carbon thereon, preferred operating conditions are temperatures of 930–970° F., pressures of 550–630 p.s.i.g. and space velocities of 2.0–4.0. It is desirable to conduct the dehydrogenation in the presence of added hydrogen.

Normally gaseous materials such as hydrogen and C_1–C_3 hydrocarbons are removed from the effluent from the dehydrogenation zone and the remaining material is then debutanized and depentanized. The resulting C_6 and heavier material or a selected fraction thereof is contacted with a solvent having an affinity for aromatics, such as, diethylene glycol, triethylene glycol or mixtures thereof, SO_2 or furfural. When the fraction which is subjected to solvent extraction has an end point of about 400° F., the solvent is preferably diethylene glycol, triethylene glycol or a mixture thereof. When the frac-

tion to be solvent extracted has an end point of from about 400–500° F. the preferred solvent is sulfur dioxide. The solvent extraction produces an extract phase rich in aromatics and a raffinate composed substantially of paraffinic hydrocarbons having a luminosity number of at least 100 and suitable for use in gas turbine engines. to obtain a fuel of particularly high luminosity number, the raffinate may be percolated over a solid adsorbent such as fuller's earth or silica gel or treated with fuming sulfuric acid to remove residual aromatics therefrom or the aromatics may be hydrogenated to naphthenes which are not as undersirable as aromatics. The resulting product has a luminosity number in excess of 125 and is particularly useful as a fuel for gas turbine engines. When the raffinate is treated with silica gel, the C_4 and C_5 hydrocarbons removed from the dehydrogenation product are advantageously used to displace periodically the adsorbed aromatics from the silica gel.

When the starting material contains relatively high amounts of sulfur or metallic impurities such as arsenic which would poison the platinum isomerization catalyst, it is desirable to pretreat the starting material with a sulfur-resistant catalyst such as cobalt molybdate on alumina or nickel-tungsten-sulfide at a temperature of about 400–850° F., a pressure of about 50–1500 p.s.i.g., a liquid hourly space velocity of about 0.5–20 in the presence of about 250–6000 s.c.f. hydrogen per barrel of feed.

For the production of fuels of even higher luminosity numbers, the feed is subjected to a preliminary dehydrogenation followed by solvent extraction prior to the isomerization step. By operating in this manner, C_6 ring naphthenes already present in the feed can be removed before the isomerization step. The preliminary dehydrogenation is preferably effected immediately prior to the isomerization step.

The invention may be better understood from the following example which is given for illustrative purposes only.

EXAMPLE I

The charge stock, a 300–500° F., cut of a crude petroleum containing 8 volume percent aromatics, 44 volume percent naphthenes and 48 volume percent paraffins and having a freezing point of —50° F., a luminosity number of 65 and an IP smoke point of 27 millimeters is passed over a cobalt molybdate on alumina catalyst at a temperature of 670° F., a pressure of 450 p.s.i.g., a space velocity of 2.5 v./v./hr. and a hydrogen to hydrocarbon mol ratio of 1.0. Separate portions of the normally liquid product are treated as tabulated below:

Table I

	Run A	Run B
Catalyst	Pt+3% F	Pt+6% F
Temperature, ° F	680	680
Pressure, p.s.i.g.	500	500
Space Vel., v./v./hr.	1.5	1.5
H_2/Hc. Ratio	4.0	4.0

The normally liquid portion of the product from each run is contacted with a catalyst containing 10% molybdena on alumina under the following conditions:

Table II

	Run A	Run B
Temperature, ° F	925	925
Pressure, p.s.i.g.	200	200
Space Vel., v./v./hr.	0.5	0.5
H_2 Partial Pressure in Reactor, Percent of total	70	70

The normally liquid product of each run is then fractionated to yield a fraction having a boiling range of 300–500° F. which is extracted with sulfur dioxide to remove the aromatics. The raffinates have the following composition:

Table III

Volume, percent	Run A	Run B
Aromatics	4.5	4.8
Naphthenes	10.3	3.4
Paraffins	85.2	91.8

The raffinates are then percolated over silica gel to yield products having the following characteristics:

Table IV

	Run A	Run B
Low Heating Value, B.t.u./lb.	18,950	19,070
IP Smoke Pt., mm.	45	50
Luminosity No.	135	162

For comparative purposes, similar characteristics for fuels currently in use as JP–4, JP–5 and jet fuel grade kerosene are reproduced below:

	JP–4	JP–5	Kerosene
Low Heating Value, B.t.u./lb.	18,735	18,619	18,430
IP Smoke Pt., mm.	25	28.7	16
Luminosity No.	72	81	36

It will be noted from the above that JP–4 and JP–5 fuels commercially in use barely meet their specifications of a minimum smoke point of 20 millimeters and the fuel used commercially for jet engines does not even meet the military specifications. In contrast, the fuels of the present invention have high smoke points ranging from 45 to higher than 50 millimeters. This is indicative of the low smoke producing characteristics of the fuels of the present invention.

It will also be noted that the fuels of the present invention have high luminosity numbers and accordingly burn with flames having low radiation characteristics, thus permitting gas turbine powered aircraft to be operated without the necessity for frequent overhauls or to be operated at increased thrust without increasing the frequency of complete overhauls due to damage to the engine parts resulting from high radiation flames.

Obviously, many modifications and variations of the invention as hereinbefore set forth may be made without departing from the spirit and scope thereof and therefore only such limitations should be imposed as are indicated in the appended claims.

I claim:

1. A process for the production of a fuel suitable for use in a gas turbine engine which comprises contacting a hydrocarbon liquid fraction containing alkyl C_5 ring naphthenes and having an initial boiling point of at least 200° F. with a desulfurization catalyst at a temperature between about 400 and 850° F., a pressure between about 50 and 1500 p.s.i.g. in the presence of hydrogen, passing the reaction product into contact with a catalyst comprising platinum on alumina and containing at least 3 percent by weight fluorine at a temperature between about 600 and 800° F., a pressure between 50 and 700 p.s.i.g. in the presence of hydrogen, subjecting the normally liquid product to dehydrogenation conditions in the presence of a dehydrogenation catalyst and extracting at least a portion of the resulting normally liquid product with a solvent having an affinity for aromatics to produce an extract phase of increased aromatic content and a raffinate consisting substantially of acyclic paraffin hydrocarbons.

2. The process of claim 1 in which C_4 and C_5 hydrocarbons are removed from the dehydrogenation product prior to the treatment of the dehydrogenation product with the solvent.

3. The process of claim 1 in which the raffinate is contacted with silica gel to remove residual aromatic compounds therefrom.

4. A process for the production of a fuel suitable for use in a gas turbine engine which comprises contacting a hydrocarbon liquid fraction containing alkyl C_5 ring naphthenes and having an initial boiling point of at least 200° F. with a desulfurization catalyst at a temperature between about 400 and 850° F., a pressure between about 50 and 1500 p.s.i.g. in the presence of hydrogen, passing the reaction product into contact with a catalyst comprising platinum on alumina and containing at least 3 percent by weight fluorine at a temperature between about 600 and 800° F., a pressure between 50 and 700 p.s.i.g. in the presence of hydrogen, subjecting the normally liquid product to dehydrogenation conditions in the presence of a dehydrogenation catalyst, debutanizing and depentanizing the dehydrogenation product, extracting the debutanized, depentanized residue with a solvent having an affinity for aromatic compounds to produce an extract phase having an increased automatic content and a raffinate composed predominantly of paraffins percolating the raffinate over silica gel to remove residual aromatics therefrom and periodically displacing adsorbed aromatics from the silica gel by light hydrocarbons removed from the dehydrogenation product.

5. A process for the production of a fuel suitable for use in a gas turbine engine which comprises contacting a hydrocarbon liquid fraction containing alkyl C_5 ring naphthenes and having an initial boiling point of at least 200° F. with a desulfurization catalyst at a temperature between about 400 and 850° F., a pressure between about 50 and 1500 p.s.i.g. in the presence of hydrogen, passing the reaction product into contact with a catalyst comprising platinum on alumina and containing about 6% by weight fluorine at a temperature between about

600 and 800° F., a pressure between 50 and 700 p.s.i.g. in the presence of hydrogen, subjecting the normally liquid product to dehydrogenation conditions in the presence of a dehydrogenation catalyst, debutanizing and depentanizing the dehydrogenation product, extracting the debutanized, depentanized residue with a solvent having an affinity for aromatic compounds to produce an extract phase having an increased aromatic content and a raffinate composed predominantly of paraffins, percolating the raffinate over silica gel to remove residual aromatics therefrom and periodically displacing adsorbed aromatics from the silica gel by light hydrocarbons removed from the dehydrogenation product.

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