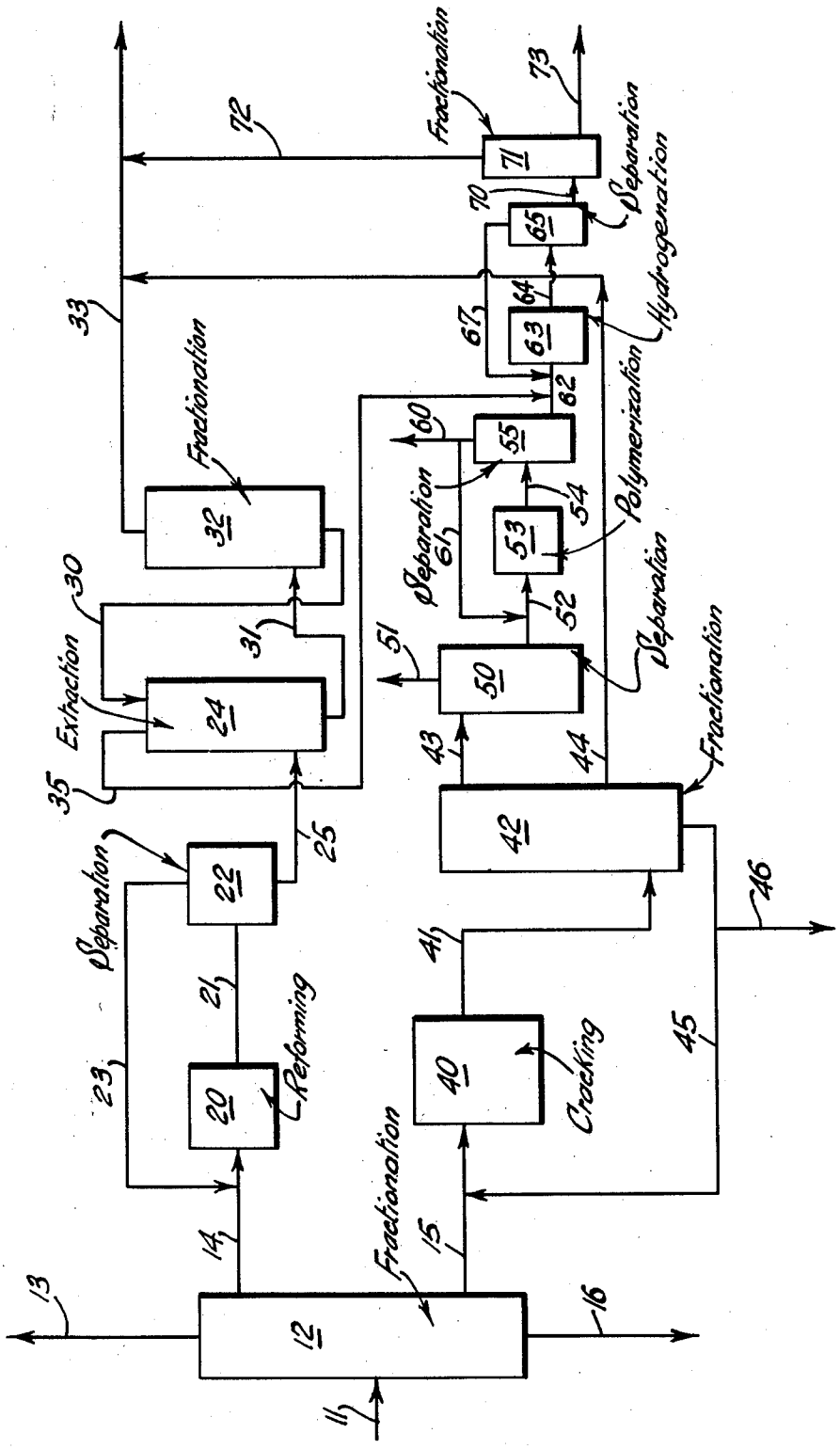
March 17, 1964 E. R. KERR ETAL 3,125,503

PREPARATION OF A JET FUEL

Filed Dec. 29, 1959



United States Patent Office 3,125,503 Patented Mar. 17, 1964

3,125,503

PREPARATION OF A JET FUEL

Edwin Robert Kerr, Fishkill, Edward R. Christensen, Wappingers Falls, William F. Franz, Hopewell Junction, and Herbert E. Vermillion, Wappingers Falls, N.Y., assignors to Texaco Inc., New York, N.Y., a corporation of Delaware

Filed Dec. 29, 1959, Ser. No. 862,592
5 Claims. (Cl. 208—79)

This invention relates to the production of gas turbine engine fuels. More particularly, it relates to the production of fuels suitable for use in jet aircraft engines. In one specific embodiment, the present invention is concerned with the simultaneous production of high octane fuel for piston engines and high luminometer number fuels for jet 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. When jet fuels prepared by the process of the present invention are used under the same conditions, the problem of excessive smoke during take-off is substantially eliminated.

Another disadvantage attached to the use of current jet engine fuels is the necessity for 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 the 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 currently 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 jet aircraft engines frequently and experience has shown that a fairly thorough overhaul is necessary after about 500–600 hours of operation.

It is an object of the present invention to provide a jet engine fuel of improved burning characteristics. Another object of the present invention is to provide a jet fuel of low aromatic hydrocarbon content. Another object of the present invention is to produce a jet fuel which burns with a flame of low luminosity. Another object of the present invention is to produce a gas turbine engine fuel which subjects the engine parts to reduced thermal stress. Another object of the present invention is to provide a process for the separate production of a

motor fuel of high octane number and a jet fuel of high luminometer number.

The luminometer number is a measure of the burning characteristics of a fuel, the higher the luminometer number the less smoke produced by the fuel during take-off and the lower the amount of radiation produced by the flame. The luminometer number may be determined using a Smoke Point Lamp described in the "Tentative Method of Test for Smoke Point of Jet Fuels," ASTM Designation D1322–54T* modified by the addition of two thermocouples, one for measuring the temperature of the incoming air, the other shielded from the flame and inserted in the chimney to measure the temperature of the combustion gases, and a radiometer adjustably positioned to measure the amount of radiation emanating from the flame.

To determine the luminometer number, several determinations are made burning tetralin in the lamp, each run being made at a different wick height, the radiometer being positioned at the zone of maximum radiation, and the amount of radiation for each run and the temperature differential between the incoming air and the combustion gases being recorded. After several runs have been made on tetralin, a curve is drawn plotting ΔT against the amount of radiation. Similar curves are then made for isooctane and the test fuel. The ΔT for each material at a selected amount of radiation, e.g. 0.3 mv., is read from the curves and is inserted in the formula:

$$\text{Luminometer number} = \frac{\Delta T \text{ (test fuel)} - \Delta T \text{ (tetralin)}}{\Delta T \text{ (isooctane)} - \Delta T \text{ (tetralin)}} 100$$

In this way the luminometer number of the test fuel can be determined.

It has been found that fuels having low luminometer numbers burn with a highly radiant flame and also produce excessive smoke during take-off. It has also been found that fuels having relatively high aromatic contents have relatively low luminometer numbers. Even fuels which meet current military jet fuel specifications have the undesirable characteristics of producing excessive smoke during take-off and of burning with flames of high radiation which are detrimental to the life of the jet engine. For example, the specifications for JP–4 and JP–5 permit a maximum aromatic content of 25%. However, jet fuels which meet this requirement are unsatisfactory in the two respects just mentioned probably for the reason that they generally contain more than 10% aromatics.

In accordance with one embodiment of the present invention, a crude oil is separated into a naphtha fraction and a heavy fraction having a boiling range of from about 390 to 760° F. The naphtha is subjected to catalytic reforming to convert the naphthenes present to aromatics which are removed from the reformate by solvent extraction. The heavy fraction is subjected to catalytic cracking and the product is separated into a C_2 and lighter gaseous fraction, a C_3–C_4 olefin containing fraction, a C_5–400° F. fraction and a 400° F.+ fraction which is recycled to the catalytic cracking operation. The C_2 and lighter fraction is removed from the system. The C_5–400° F. fraction may be processed further as, for example, by catalytic reforming or it may be separated into a C_6–C_7 fraction which is isomerized and the balance reformed or it may be combined in its entirety with the aromatic extract recovered from the reformate. The C_3–C_4 olefin containing fraction is subjected to a polymerization reaction and the resulting liquid polymer together with the non-aromatic portion of the reformate is hydro-

*ASTM Standards on Petroleum Products and Lubricants, published 1956 by the American Society for Testing Materials.

genated to produce a jet fuel of improved burning characteristics.

The reforming is ordinarily conducted in the presence of a reforming catalyst, such as a platinum on alumina catalyst which may or may not contain combined halogen. Molybdena-alumina catalysts are also satisfactory for this purpose. The reforming is conducted at a temperature of from about 850–950° F. and a pressure of about 500 p.s.i.g. Hydrogen is recycled at the rate of about 8000 cubic feet per barrel of liquid feed. The reformate, i.e., the normally liquid product recovered from the reforming reaction is then subjected to a treatment which separates the aromatic constituents from the paraffinic constituents. This may be effected by treatment with a solid adsorbent such as silica gel or the separation may be effected by the use of a selective solvent such as SO_2, furfural, ethylene glycol, diethylene glycol, triethylene glycol or mixtures of glycols. Preferably, the separation is effected by the use of a glycol solvent.

The 390–760° F. fraction is preferably contacted with a fluidized bed of silica-alumina or silica-magnesia catalyst at a temperature between about 880 and 980° F. and a pressure between about 10 and 18 p.s.i.g. Space velocities will range from 1.0–3.0 weight of feed per hour per weight of catalyst with a catalyst to oil ratio of 8–12/1.

The C_3–C_4 olefin containing fraction recovered from the cracking zone effluent is then contacted with an acidic polymerization catalyst such as copper pyrophosphate, boron fluoride, aluminum chloride or phosphoric acid supported on an inert material such as quartz or kieselguhr. The polymerization, when a phosphorus-containing catalyst is used, is generally conducted at a temperature between about 300 and 500° F., a pressure between 150 and 1500 p.s.i.g. The liquid polymer is then combined with the non-aromatic portion of the reformate and the combined stream is subjected to hydrogenation for the saturation of the polymer and also to convert residual aromatics present in the non-aromatic portion of the reformate to naphthenes.

Ordinarily, the hydrogenation is conducted in the presence of a hydrogenation catalyst. Suitable hydrogenation catalysts are platinum, palladium and nickel and the oxides or sulfides of metals such as molybdenum, chromium, cobalt and tungsten. These catalytic materials may be supported on materials such as alumina, silica-alumina, kieselguhr and the like. Since platinum, palladium and nickel are sensitive to sulfur compounds which may be present in the feed, it is advisable when it contains a substantial amount of sulfur to pretreat the feed prior to subjecting it to contact with the platinum, palladium or nickel catalyst. A suitable treatment comprises contacting the feed with a cobalt molybdate on alumina or a nickel tungsten sulfide catlayst in the presence of hydrogen at a temperature ranging from about 400° F. to 900° F., preferably 500° F. to 800° F. and a pressure of about 100 p.s.i.g. to 1000 p.s.i.g., preferably 200–750 p.s.i.g.

Hydrogenation of the aromatics to naphthenes should be carried out at a temperature of not more than 700° F. Preferred temperatures range from 500 to about 675° F. When the reaction temperature exceeds 700° F., the reaction reverses and instead of the desired hydrogenation of aromatics to naphthenes taking place, the naphthenes present are dehydrogenated to aromatics. Pressures should be maintained above 250 p.s.i.g., preferred operating pressures being 250–750 p.s.i.g. Space velocities may range from about 0.2 to 10 volumes of feed per volume of catalyst per hour, a preferred range being from 0.5 to 4 v./v./hr. Hydrogen rates of 1000 to 20,000 s.c.f./bbl. may be used although rates of 5000 to 15,000 s.c.f./bbl. are preferred.

The invention may be better understood by reference to the attached drawing which shows diagrammatically a flow scheme for the practice of one embodiment of the present invention and in connection with which a specific example is described.

A crude oil is introduced through line **11** into fractionator **12** where it is separated into a normally gaseous portion withdrawn through line **13**, a C_5–390° F. fraction withdrawn through line **14**, a 390–760° F. fraction withdrawn through line **15** and a residual fraction withdrawn through line **16**. Although this separation is indicated as taking place in one vessel, it will be obvious to those skilled in the art that the separation is actually made serially in two vessels, the first operated at atmospheric pressure and the second at subatmospheric pressure.

The C_5–390° F. fraction is contacted in reactor **20** with a platinum alumina combined halogen catalyst at a temperature of 900° F., a pressure of 500 p.s.i.g., a space velocity of 3.0 volumes of feed per volume of catalyst per hour and a hydrogen recycle rate of 10,000 cubic feet per barrel. The reaction products are then transferred to separation zone **22** through line **21**. In separation zone **22** hydrogen is removed from the product stream and is recycled to reforming zone **20** through lines **23** and **14**. The normally liquid portion of the reformate is then sent to extraction zone **24** through line **25** in which zone it is countercurrently contacted with a glycol solvent introduced through line **30**. The aromatic containing extract is removed from extraction zone **24** through line **31** and is introduced into fractionation zone **32** where the aromatic rich extract is separated from the solvent and removed as overhead through line **33**. The essentially aromatic free solvent is removed from fractionation zone **32** and recycled to extraction zone **24** through line **30**. The low aromatic raffinate which contains about 95% paraffins and small amounts of olefins, naphthenes and aromatics is removed from extraction zone **24** through line **35**. Before being subjected to further treatment, the raffinate is advantageously contacted in a vessel (not shown) with, for example, water, to remove residual amounts of solvent which may be present.

The 390–760° F. fraction is introduced into catalytic cracking zone **40** wherein it is contacted with a fluidized bed of silica-alumina catalyst at a temperature of 925° F. and a pressure of 15 p.s.i.g. The space velocity is 2.2 weight of feed per hour per weight of catalyst and the catalyst to oil ratio is 9.5. The reaction products are sent from catalytic cracking zone **40** through line **41** to fractionation zone **42** from which gaseous material up through C_4 hydrocarbons is removed through line **43**, a C_5–400° F. fraction is removed through line **44** and the 400° F.+ fraction is recycled to catalytic cracking zone **40** through lines **45** and **15**. Excess recycle is withdrawn from the system through line **46**. The C_5–400° F. fraction is combined with the aromatic rich extract in line **33**.

The C_4 and lighter fraction is then sent through line **43** to separation zone **50** from which C_2 and lighter material is removed through line **51**. The C_3–C_4 fraction is transferred via line **52** to polymerization zone **53** where it is contacted with a phosphoric acid on kieselguhr catalyst at a temperature of 420° F., a pressure of 700 p.s.i.g. and a space velocity of 0.25 liquid gallon of feed per hour per pound of catalyst. Effluent from polymerization reactor **53** is passed through line **54** to fractionator **55** from which gaseous material is removed through line **60**. If desired, gaseous material may be recycled through lines **61** and **52** to polymerization reactor **53** but in this example it is withdrawn from the system in its entirety. The normally liquid polymer is withdrawn from fractionator **55** through line **62** where it is combined with the low aromatic portion of the reformate withdrawn from extractor **24** through line **35**. The combined stream is introduced into hydrogenation zone **63** where it is contacted with a nickel oxide on kieselguhr catalyst at a temperature of 500° F., a pressure of 750 p.s.i.g., a space velocity of 1.0 volume of feed per hour per volume of

catalyst and a hydrogen feed rate of 12,000 cubic feet per barrel of feed. The effluent from hydrogenation zone 63 passes through line 64 to separator 65 in which hydrogen-containing gas is removed from the effluent and recycled to hydrogenation zone 63 through lines 67 and 62. Normally liquid hydrogenation product is then sent through line 70 to fractionator 71 where it is separated into a fraction boiling below 200° F. and a fraction boiling above 200° F., the lighter fraction being combined by means of line 72 with the extract and cracked gasoline in line 33 to yield a motor fuel having an ASTM Research Octane Number of 91 clear, 97 leaded. The heavier fraction withdrawn through line 73 has a luminometer number of 120 and is admirably suited for use alone or in combination with other materials as a jet fuel.

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.

We claim:

1. A process for the production of an improved jet fuel which comprises fractionating a crude petroleum into a first liquid fraction having a distillation end point of about 390° F. and a second liquid fraction boiling within the range of about 390–760° F., reforming said first liquid fraction to produce a reformate of increased aromatic content, separating said reformate into a portion rich in aromatics and a non-aromatic portion, contacting said second liquid fraction with a cracking catalyst under cracking conditions to produce a cracked product, separating the cracked product into a C_3–C_4 olefin-containing fraction and a cracked naphtha fraction, subjecting said C_3–C_4 olefin-containing fraction to polymerization conditions in the presence of a polymerization catalyst to produce a normally liquid polymer, combining said normally liquid polymer and said non-aromatic portion, contacting the combined stream with a hydrogenation catalyst in the presence of 5,000–15,000 s.c.f. hydrogen per barrel under saturation conditions and recovering a hydrocarbon fraction boiling in the jet fuel range from the hydrogenation product.

2. The process of claim 1, in which the cracked naphtha is combined with the first liquid fraction and the combined stream is reformed.

3. A process for the production of an improved jet fuel and the simultaneous production of a high octane motor fuel which comprises fractionating a crude petroleum into a first liquid fraction having a distillation end point of about 390° F. and a second liquid fraction boiling within the range of about 390–760° F., reforming said first liquid fraction to produce a reformate of increased aromatic content, separating said reformate into a portion rich in aromatics and a non-aromatic portion, contacting said second liquid fraction with a cracking catalyst under cracking conditions to produce a cracked product, separating the cracked product into a C_3–C_4 olefin-containing fraction and a cracked naphtha fraction, subjecting said C_3–C_4 olefin-containing fraction to polymerization conditions in the presence of a polymerization catalyst to produce a normally liquid polymer, combining said normally liquid polymer and said non-aromatic portion, contacting the combined stream with a hydrogenation catalyst in the presence of 5,000–15,000 s.c.f. hydrogen per barrel under saturation conditions and recovering a hydrocarbon fraction boiling in the jet fuel range from the hydrogenation product, and combining the cracked naphtha with the portion of increased aromatic content to produce a high octane motor fuel.

4. A process for the production of an improved jet fuel and the simultaneous production of a high octane motor fuel which comprises fractionating a crude petroleum into a first liquid fraction having a distillation end point of about 390° F. and a second liquid fraction boiling within the range of about 390–760° F., reforming said first liquid fraction to produce a reformate of increased aromatic content, separating said reformate into a portion rich in aromatics and a non-aromatic portion, contacting said second liquid fraction with a cracking catalyst under cracking conditions to produce a cracked product, separating the cracked product into a C_3–C_4 olefin-containing fraction and a cracked naphtha fraction, subjecting said C_3–C_4 olefin-containing fraction to polymerization conditions in the presence of a polymerization catalyst to produce a normally liquid polymer, combining said normally liquid polymer and said non-aromatic portion, contacting the combined stream with a hydrogenation catalyst in the presence of 5,000–15,000 s.c.f. hydrogen per barrel under saturation conditions, fractionating the hydrogenation product into a liquid fraction boiling below about 200° F. and a fraction boiling in the jet fuel range and combining said fraction boiling below about 200° F., said cracked naphtha and said fraction rich in aromatics to produce a motor fuel of high octane number.

5. A process for the production of an improved jet fuel and the simultaneous production of a high octane motor fuel which comprises fractionating a crude petroleum into a first liquid fraction having a distillation end point of about 390° F. and a second liquid fraction boiling within the range of about 390–760° F., reforming said first liquid fraction to produce a reformate of increased aromatic content, separating said reformate into a portion rich in aromatics and a non-aromatic portion, contacting said second liquid fraction with a cracking catalyst under cracking conditions to produce a cracked product, separating the cracked product into a C_3–C_4 olefin-containing fraction and a cracked naphtha fraction, subjecting said C_3–C_4 olefin-containing fraction to polymerization conditions in the presence of a polymerization catalyst to produce a normally liquid polymer, combining said normally liquid polymer and non-aromatic said portion, contacting the combined stream with a hydrogenation catalyst in the presence of 5,000–15,000 s.c.f. hydrogen per barrel under saturation conditions, fractionating the hydrogenation product into a liquid fraction boiling below about 200° F. and a jet fuel fraction boiling above about 200° F. and combining said fraction boiling below about 200° F. with said portion rich in aromatics to produce a motor fuel of high octane number.

References Cited in the file of this patent

UNITED STATES PATENTS

2,285,785	Seguy	June 9, 1942
2,332,563	Egloff	Oct. 26, 1943
2,349,160	Frey et al.	May 16, 1944
2,354,866	Lang	Aug. 1, 1944
2,472,494	Slotterbeck	June 7, 1949
2,671,754	De Rosset et al.	Mar. 9, 1954
2,943,038	Hansen	June 28, 1960
2,945,802	Ciapetta et al.	July 19, 1960
2,956,002	Folkins	Oct. 11, 1960
3,000,815	Heney	Sept. 19, 1961