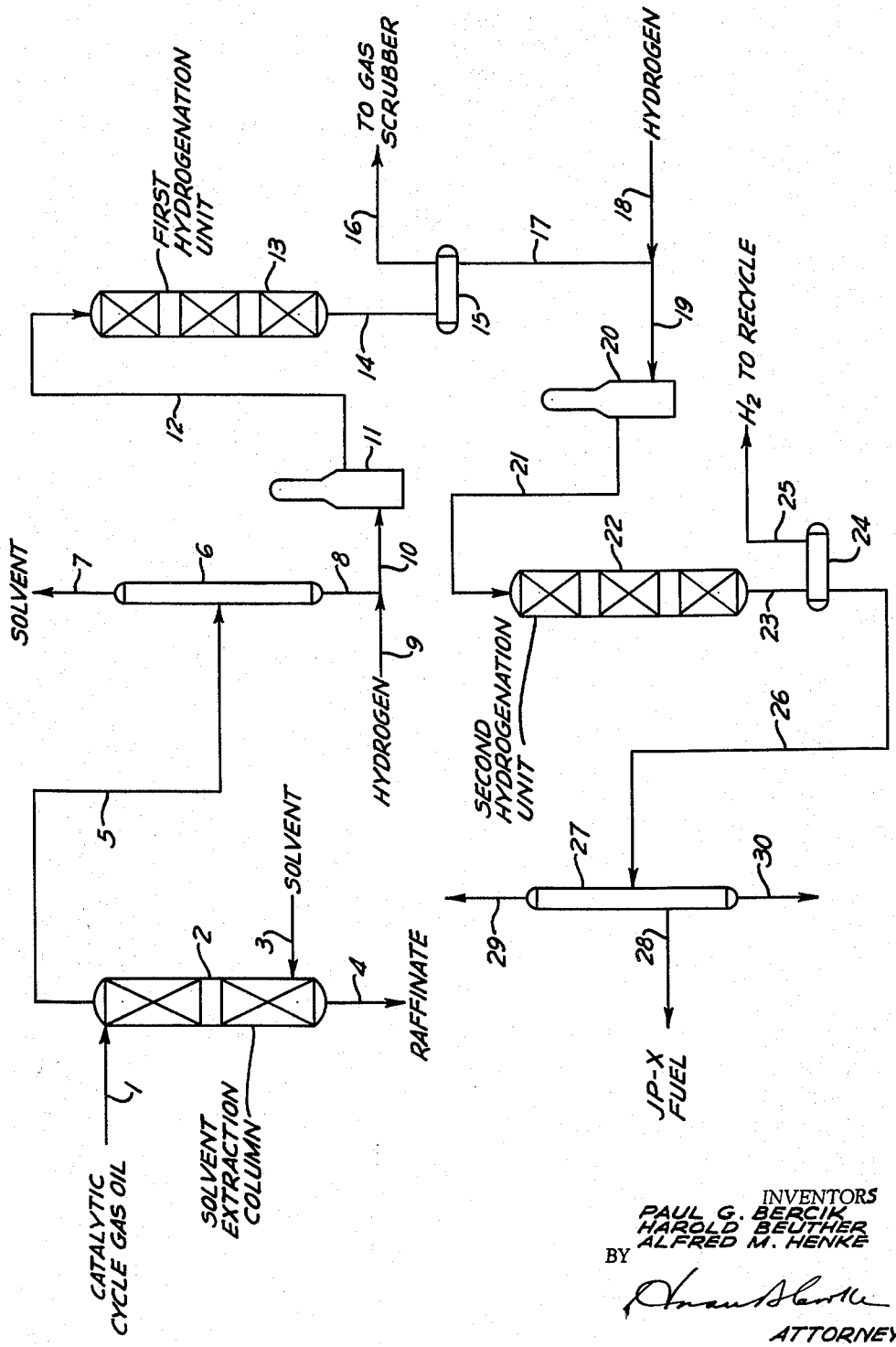
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PROCESS FOR PREPARING A JET FUEL

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INVENTORS
PAUL G. BERCIK
HAROLD BEUTHER
ALFRED M. HENKE

BY

ATTORNEY

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PROCESS FOR PREPARING A JET FUEL

Paul G. Bercik, Glenshaw, Harold Beuther, Gibsonia, and Alfred M. Henke, Springdale, Pa., assignors to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

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3 Claims. (Cl. 208—212)

This invention relates to a process for making fuels for jet engines and more specifically jet fuels which have been termed "JP–X Fuels."

The JP–X Fuels must have the following properties: A net heat of combustion of over 18,350 B.t.u.'s per pound of the fuel and over 135,000 B.t.u.'s per gallon of the fuel. Further, fuels of this class must have good low temperature fluidity properties, below —40° F. freeze point and excellent thermal stability. It is apparent that the production of fuels meeting these specifications presents a difficult problem, particularly when it is recognized that the fuels must be made at a reasonable cost.

We have discovered in accordance with the invention that fuels meeting these specifications can be prepared efficiently by the process described more fully hereinafter. The charge stock for the process is a catalytic cycle gas oil formed when heavier oils are cracked in conventional catalytic cracking units. In the present process the cycle gas oil is fractionated to obtain a fraction having an initial boiling point of at least about 475° F., a 50 percent point above about 550° F., a 75 percent point above about 675° F. and an end point lower than about 715° F. Cycle gas oils of this type contain a high percentage of aromatic hydrocarbons. We have found that an excellent jet fuel can be obtained using a cycle gas oil of the boiling ranges referred to above and employing a process involving additionally a solvent extraction of the cycle gas oil and subjecting the extract to a hydrogenation pretreatment to reduce substantially the sulfur and nitrogen content of the extract. The extract, after removal of sulfur and nitrogen, is subjected to a saturative hydrogenation treatment to convert the aromatic hydrocarbons to saturated condensed ring hydrocarbons.

The invention will be understood more clearly by reference to the accompanying drawing which is a flow diagram illustrating a preferred manner of carrying out the process of the invention. Referring to the drawing, a fraction of cycle oil as described above is flowed through line 1 to a solvent extraction column 2. Solvent is introduced into the column through line 3. The raffinate is withdrawn from the bottom of column 2 through line 4 and may be processed for recovery of solvent. The extraction is carried out so as to obtain an extract yield equal to or less than the aromatic content of the cycle oil and for best results the extraction is carried out so as to obtain an extract yeld of about 5 to about 20 percent by volume less than the aromatic content of the cycle oil. Under these conditions, extracts composed of 90 to 97 percent aromatics can be obtained.

The solvent extract stream is withdrawn through line 5 and fed to a distillation column 6 where the solvent is evaporated and withdrawn through line 7. The extract is withdrawn as bottoms from distillation column 6 through line 8. The extract is then mixed with hydrogen introduced through line 9 and the mixture is flowed through line 10 to heater 11. The resulting mixture is flowed through line 12 to a first catalytic hydrogenation unit 13, wherein the extract is subjected to a relatively mild catalytic hydrogenation effective however to reduce the nitrogen and sulfur content of the extract to a low level. We have found that if the sulfur and/or nitrogen content of the treated extract is too high, the catalyst employed for the saturative hydrogenation will be rapidly

deactivated and the fuel produced will have poor stability, owing to relatively high aromatic, sulfur and nitrogen contents. In accordance with the invention the first hydrogenation is preferably carried out so as to reduce the sulfur in the extract to less than 150 p.p.m. and the nitrogen content to less than 30 p.p.m. The treated product, together with excess hydrogen, is removed from the bottom of catalytic hydrogenation unit 13 through line 14 to a conventional separator 15 in which excess gas is separated from the hydrogenated extract. Excess gas is removed through line 16 to a gas scrubber, not shown. After the separation, the treated extract is flowed through line 17 in admixture with hydrogen introduced through line 18 and the mixture is introduced through line 19 into a heater 20. The heated product is then flowed through line 21 into a second catalytic hydrogenation unit 22. This hydrogenation unit is operated so as to saturate the aromatic hydrocarbons in the extract. The hydrogenated extract is withdrawn from the hydrogenation unit through line 23 to a separator 24 from which excess hydrogen is removed through line 25 and may be used as recycle to the hydrogenation units. The substantially completely hydrogenated product is removed from the separator through line 26 to a fractionator 27 and the JP–X Fuel is removed from the fractionator through line 28 and thence to storage. Lighter and heavier fractions are withdrawn through lines 29 and 30, respectively.

In order to describe the invention more clearly, it is pointed out that there are five main elements making up the process. The first is the selection of the charge stock. While any cycle oils having the properties within the ranges heretofore described are satisfactory charge stocks for the process, we prefer in accordance with the invention to employ cycle oils or fractions of such oils having initial boiling points higher than about 500° F., a 50 percent point higher than about 600° F., a 75 percent point less than about 650° F. and an end point less than about 690° F. Use of cycle stocks having these inspections results in jet fuels having good volumetric heats of combustion and low freezing points, and, in addition, the yields of the fuels are excellent.

The invention will be understood more fully by reference to the following example.

Example

The catalytic cycle oil treated in this example had approximately the following composition, percent by weight:

515–600° F.	50.0
600–650° F.	37.5
650–685° F.	12.5

This cycle oil was subjected to solvent extraction with acetonitrile as the solvent. The volume ratio of the solvent and cycle oil was 1:1 and the extraction was carried out at a temperature of 80° F. The extract was then subjected to catalytic hydrogenation which reduced substantially the nitrogen and sulfur in the extract. The catalyst employed in this hydrogenation was a nickel tungsten catalyst on an alumina non-cracking base. 32 percent of the catalyst was composed of equal parts of nickel and tungsten, the rest being the alumina base. The hydrogenation was carried out at a temperature of about 723° F., a pressure of about 1000 pounds per square inch gauge, and a hydrogen circulation rate of 4000 s.c.f./bbl. The liquid space velocity, volume per volume per hour, was 0.5.

The treated extract substantially free of nitrogen and sulfur was then subjected to a less severe hydrogenation which was effective to saturate the aromatic hydrocarbons. The catalyst employed in this phase of the process was a catalyst comprising nickel deposited on keiselguhr in which 48 percent by weight of the catalyst was

nickel. This hydrogenation was carried out at a temperature of 575° F., a pressure of 1000 p.s.i.g. and a hydrogen circulation rate (standard cubic feet per barrel) of 8000. The liquid space velocity, volume per volume per hour, was 0.5. The product yield, percent by volume of the cycle oil, was as follows:

Extract	50.2
Raffinate	49.8
425–600° F. JP–X Fuel	44.6
350–425° F. jet fuel	10.0
600° F.+ fuel	2.2
180–350° F. gasoline	2.6

In the following table the product inspections are set out.

Product Inspections, Description	Cycle Oil	Extract	First Hydrogenation	Final Hydrogenation	425–600° F., JP–X	350–254° F., Jet Fuel
Aromatics, percent by Vol	55.0	92.3	62.5	1.5	2.8	1.9
Heat of Combustion, Net:						
B.t.u./lb					18,404	18,542
B.t.u./gal					135,269	131,371
Freeze Point; ° F					−60	<−76
Sulfur, percent	1.28	2.12	.003			
Nitrogen, percent	0.035	0.055	<.003			

A fuel prepared in accordance with the example was tested to determine its thermal stability. The test employed was the CFR Fuel Coker Test Procedure. This test procedure is described in detail in the Manual of ASTM Standards on Petroleum Products, ASTM D–1660–59T. In accordance with this test method, aviation turbine fuels are subjected to flow conditions and temperature stresses similar to those in combustion gas turbine or jet aircraft engines by circulation through a simulated aircraft fuel system at a temperature above 300° F., at a rate of 6 pounds of fuel per hour, for a period of 300 minutes. The test apparatus comprises a fuel system containing two heated sections, one of which is a preheater section that simulates the hot fuel line sections of an aviation turbine engine as typified by the engine fuel lubricating oil cooler. The extent of fouling of heat transfer surfaces in the preheater section by fuel degradation deposits is determined by inspection and the extent of such fouling is used as one index of the temperature stability of the aviation turbine engine. Preheater deposits are rated according to the following scale: 0=no visible deposits; 1=visible haze or dulling, but no visible color; 2=barely visible coloration; 3=light tan to peacock stain; 4=heavier than 3.

The second heated section comprises a filter section that simulates the nozzle area or fuel inlet area of the combustion zone of a jet engine where fuel degradation particles may be trapped. A precision, sintered stainless steel filter is employed in the filter to trap fuel degradation particles formed during the test. The extent of the build-up of fuel degradation particles in the filter section is indicated by the pressure differential across the filter and this pressure differential is used as another index of the high temperature stability of the aviation turbine fuel. In carrying out the test described, the temperature of the fuel at the outlet of the preheater section was maintained at 450° F. and the filter temperature was maintained at 500° F.

The results of this test were the following: The filter pressure drop in inches of mercury was 0.1 and the preheater deposits were zero.

It will be understood that changes can be made in the process described in the example without departing from the scope of the invention. In the solvent extraction step of the process, other solvents can be employed in place of acetonitrile; for example, furfural, sulfur dioxide, ammonia and ethylene glycol can be employed.

For the first hydrogenation of the extract any of the familiar hydrogenation catalysts can be used, provided the catalyst does not have strong catalytic cracking properties at the hydrogenation conditions employed. For example, catalysts comprising one or more metals such as cobalt, nickel, molybdenum, or tungsten deposited on a non-cracking base can be used. Further, it will be understood that the temperatures for this operation can be varied, depending upon the charge stock. For example, temperatures within the range of about 600° to 800° F. can be used. Also, the pressure employed in this operation can be varied within the range of 500 to 5000 p.s.i.g. and space velocities within the range of 0.2 to 3.0 can be used, depending upon the other variables. Further, the hydrogen circulation rate can be varied over the range 2500 to 10,000 standard cubic feet of hydrogen per barrel.

As stated heretofore, the second hydrogenation is designed to convert the aromatic extract to a product composed substantially of saturated condensed ring hydrocarbons. While the catalyst employed in the specific example is a highly efficient catalyst for this purpose, it should be recognized that other hydrogenation catalysts can be employed to achieve good results. Some examples of such catalysts are 0.5 to 5 percent palladium or platinum supported on alumina and 15 percent to 50 percent nickel supported on alumina.

Further, the process conditions for the second hydrogenation can be varied. For example, depending upon the other variables, the temperature may be between about 400° to 700° F., the pressure may range from about 500 to about 5000 p.s.i.g., and the hydrogen circulation rate may vary between about 2500 to 10,000 standard cubic feet of hydrogen per barrel. The space velocity employed may, for example, be in the range of about 0.2 to 3.

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 of making a hydrocarbon composition adapted to be employed as a jet fuel which comprises fractionating a catalytic cracking cycle oil to obtain a fraction containing nitrogen and sulfur and having an initial boiling point more than 475° F., a 50 percent point more than 550° F., a 75 percent point less than 675° F. and an end point less than 715° F., solvent extracting said fraction, recovering the extract, reducing the sulfur and nitrogen content of said extract by catalytic hydrogenation, catalytically hydrogenating the resulting composition to saturate said composition, fractionating the resulting hydrogenated composition, and recovering from said hydrogenated composition a fuel having a net heat of combustion of more than 18,350 B.t.u.'s per pound and more than 135,000 B.t.u.'s per gallon of the fuel.

2. A process of making a hydrocarbon composition adapted to be employed as a jet fuel which comprises fractionating a catalytic cracking cycle oil to obtain a fraction having an initial boiling point of at least about

500° F., a 50 percent point more than about 600° F., a 75 percent point less than 650° F. and an end point less than 690° F., solvent extracting said fraction, recovering the extract, reducing the sulfur and nitrogen content of said extract by catalytic hydrogenation, catalytically hydrogenating the resulting composition to saturate said composition, fractionating the resulting hydrogenated composition, and recovering from said hydrogenated composition a fuel having a net heat of combustion of more than 18,350 B.t.u.'s per pound and more than 135,000 B.t.u.'s per gallon of the fuel.

3. A process of making a hydrocarbon composition adapted to be employed as a jet fuel which comprises fractionating a cycle oil from catalytic cracking to obtain a fraction containing nitrogen and sulfur and having an initial boiling point more than 475° F., a 50 percent boiling point more than 550° F., a 75 percent boiling point less than 675° F. and an end point less than 715° F., solvent extracting said fraction, recovering the extract, reducing the sulfur and nitrogen content of said extract by catalytic hydrogenation, catalytically hydrogenating the resulting composition to saturate said composition, fractionating the resulting hydrogenated composition, and recovering from said hydrogenated composition a fuel adapted for use as a jet fuel.

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ALPHONSO D. SULLIVAN, *Primary Examiner.*

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,175,970 March 30, 1965

Paul G. Bercik et al.

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 55, for "yeld" read -- yield --; columns 3 and 4, in the table, heading to the seventh column thereof, for "350-254°" read -- 350-425° --.

Signed and sealed this 17th day of August 1965.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

EDWARD J. BRENNER
Commissioner of Patents