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(54) Process for the preparation of aviation turbine fuel

(57) A process for the preparation of aviation turbine fuel hydrotreating of FCC heavy gasoline feedstock to produce a product being useful as aviation turbine fuel, comprising the step of contacting the feedstock in the presence of hydrogen with a catalyst having at least one metal of Group VIII in the Periodic Table as its active ingredient supported on a carrier, wherein the carrier comprises a crystalline alumina silicate.

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Description

The present invention is directed to the preparation of aviation turbine fuel, and, more particular, to a process for the preparation of such fuel by upgrading of FCC heavy gasoline.

FCC heavy gasoline is produced by fluid catalytic cracking of vacuum distillates and boils in the range of 100-300°C. FCC heavy gasoline has a high content of aromatics and olefins, which makes it unsuitable for aviation turbine fuel.

Aviation turbine fuel composition characteristics include a maximum content of aromatic compounds of 20 per cent by volume, a smokepoint of 20 at a minimum and a final boiling point of not higher than 300°C.

Aviation turbine fuels are conventionally prepared by upgrading middle distillate feedstock, in particular kerosene by applying a two stage hydrogenation process.

The conventional process consists of four main sections, initial hydrotreating, intermediate stripping, final hydrotreating and product stripping.

In the initial hydrotreating section, sulphur and nitrogen levels are reduced to levels that allow a catalyst in the final hydrotreater to achieve the required degree of aromatic saturation. Some aromatics conversion might occur in this section, but for the most part two and three ring aromatics are converted to single ring aromatics. The reactor will normally contain several beds of a metal sulphide catalyst, such as CoMo, NiMo or NiW on alumina. Most or all hydrogenation of olefins occurs in this stage. Quenching by treat-gas, make-up gas or by feedstock may be employed.

The reactor effluent is cooled, and gas and liquid are separated. The liquid is passed to an intermediate stripper, where dissolved H_2S and NH_3 are stripped off using either steam or recycle hydrogen.

The final hydrotreating is performed using a process layout similar to that of the initial hydrotreater. The reactor contains typically several beds of a sulphur and nitrogen sensitive noble metal catalyst.

Temperature control in the final hydrotreater can be achieved using interbed quenching by cold treat-gas, make-up gas, feed oil or product oil.

The product stripper column removes H_2S, dissolved gases and any naphtha formed in the process.

Due to high sensitivity to sulphur and nitrogen compounds, the conventional hydrogenation process is presently limited to feedstocks with a low content of those compounds.

To meet low sulphur and nitrogen specification required in the final hydrotreating step, the known processes have to date been exclusively applied to aromatics saturation of light straight-run hydrocarbon feedstocks.

It has now been found that catalytic hydrogenation may be applied for upgrading of low value FCC heavy gasoline to high value aviation turbine fuel, when employing in the final hydrotreating step of a hydrogenation process a Group VIII metal catalyst supported on a carrier comprising a crystalline alumina silicate.

Accordingly, this invention provides a process for the hydrotreating of FCC heavy gasoline feedstock comprising the step of hydrogenating aromatic compounds in the feedstock by contacting the feedstock in the presence of hydrogen with a catalyst having at least one metal of group VIII in the Periodic Table as its active ingredient supported on a carrier comprising a crystalline alumina silicate.

Group VIII metals being active as catalyst in the above process comprise preferably of platinum and/or platinum and palladium. Further active hydrogenation catalysts from Group VIII metals are ruthenium, rhodium, osmium, and iridium.

Most active catalysts for use in the process are obtained with the above supported catalysts having platinum at a concentration of between 0.1% and 0.6% by weight and palladium in the range of between 0.1% and 1.0% by weight.

It is, furthermore, preferred to use a carrier being composed of 20-100% by weight of the crystalline alumina silicate and up to 80% by weight of alumina, silica alumina or clay minerals. Presently, most preferred catalysts consist of 0.2-0.8% by weight of palladium and 0.2-0.5% by weight of platinum supported on a carrier with 30-70% by weight of zeolitic material as the crystalline alumina silicate, the zeolitic material having a unit cell size of 24.30-24.40 Å and 30-70% by weight of alumina.

Suitable methods for preparing the above hydrogenation catalysts comprise any of the known methods for the preparation of supported catalysts, including impregnation or ion-exchange of the carrier or of the crystalline alumina-silica prior to incorporation in the carrier with a solution of salts of the active metal or metals and subsequent calcination of the carrier.

Beside of being applicable for upgrading low value FCC heavy gasoline to high value aviation turbine fuel, a further advantage of the inventive process is a much lower sensitivity to sulphur and nitrogen compounds in the feedstock, which allows the process to be operated at less severe conditions and at high space velocity or reduced catalyst volume.

In operating the process of the invention, FCC heavy gasoline feedstock is desulphurized and denitrogenated in an initial hydrotreating step to levels of less than 500 ppm by weight S and less than 50 ppm by weight N by contact with a conventional high activity desulphurization catalyst, as the known NiMo, NiW or CoMo catalysts mentioned above.

After cooling, gas separation, and stripping off dissolved H_2S and NH_3 the treated feedstock is then passed to the hydrotreating step and hydrogenated with hydrogen at a H_2/oil ratio of between 100-1000 Nm^3/m^3 and hydrogen partial pressure of 10-90 atm, preferably 20-50 atm. The feedstock is contacted with the catalyst arranged as fixed bed in the hydrogenation reactor at 190-340°C, preferably 210-290°C weight average bed temperature and a pressure of 25-60 atm.

At the above conditions and a space velocity of between 0.4-10 m^3 oil/m^3 cat./h, it is possible to upgrade FCC heavy gasoline feedstock to meet the specifications of aviation turbine fuel.

Example 1

Preparation of a Pd/Pt hydrogenation catalyst supported on a zeolite/alumina carrier according to the invention.

The catalyst carrier was prepared by mixing 69 g of Catapal B (Vista Corporation), 1.3 g of 65% HNO_3 and 70 g of water. To 97.7 g of the gel prepared were added 14 g Catapal B and 70 g of dried CBV 600 HY Zeolite available from P.Q. Zeolites, having a unit cell size of 24,34 Å and a SiO_2/Al_2O_3 = 5.5. The components were thoroughly mixed in a Z-kneader until a pasta was formed. The pasta was then extruded to 1/32" extrudates. After extrusion, the wet extrudates were dried at room temperature for 16 hours, and the dried extrudates calcined at least 250°C for 2 hours in a laboratory furnace.

The calcined carrier was then impregnated by pore volume filling with an impregnation solution containing 0.6 g of $Pt(NH_2)_4(HCO_3)_2$ and 1.4 g of $Pd(NH_3)_4(HCO_3)_2$ and distilled water up to 60 ml. After impregnation, the catalyst was dried at room temperature for 16 hrs. The dried impregnated catalyst was then calcined in air at 310°C for 2 hours.

Example 2

FCC heavy gasoline having a composition as summarized in Table 1 below was in a first step subjected to desulphurization and denitrogenation by hydrotreating in an isothermal bench-scale reactor being loaded with 75 cc of a NiMo based conventional HDS catalyst, commercial available from Haldor Topsøe A/S under the tradename TK-525.

At hydrotreating conditions as summarized in Table 2, a hydrotreated product was obtained having the properties as specified in Table 3.

Table 1

FCC Heavy Gasoline Composition	
FIA Aromatics, Vol%	51.1
Olefins	34.3
Paraffins	9.9
HPLC Aromatics, Vol%	
Mono-	38.8
Di-	5.5
Tri-	0.5
Sulphur, wt%	0.268
Nitrogen, wppm	266
ASTM D-86 Distillation, °C	
IBP	128
10%	168
30%	184
50%	196
70%	210
90%	238
FBP	263

Table 2

Test Conditions	
Temperature, °C	325-328
Pressure, ato	35
LHSV, h^{-1}	3.0
H_2/Oil ratio, Nl/l	600

Table 3

Product at Test Conditions	
HPLC Aromatics, Vol%	
Mono-	45.7
Di-	0.2
Tri-	0.1
Sulphur, wppm	24
Nitrogen, wppm	4
Simulated TBP Dist., °C	
10%	149
30%	177
50%	197
70%	213
90%	238

The product collected was used for aromatics saturation using the catalyst as prepared under Example 1. The hydrodearomatization was conducted in an isothermal bench-scale reactor with a volume of 50 cc.

The conditions for aromatics saturation and the corresponding properties are shown in Table 4 and Table 5, respectively.

Table 4

Test Conditions	
Temperature, °C	242
Pressure, ato	35
LHSV, h^{-1}	1.0
H_2/oil ratio, Nl/l	600

Table 5

Product Properties	
HPLC Aromatics, vol%	
Mono-	5.5
Di-	0.1
Tri-	0
Simulated TBP Dist, °C	
10%	145
30%	172
50%	189
70%	204
90%	231
Smoke Point, mm	23

Claims

1. A process for the preparation of aviation turbine fuel by hydrotreating of a FCC heavy gasoline feedstock, comprising the step of hydrogenating aromatic compounds in the feedstock by contacting the feedstock in the presence of hydrogen with a catalyst having at least one metal of Group VIII in the Periodic Table as its active ingredient supported on a carrier, comprising a crystalline alumina silicate.

2. The process of claim 1, wherein the Group VIII metal comprises platinum and/or palladium.

3. The process of claim 1, wherein the Group VIII metal is supported in an amount of between 0.3 and 0.5% by weight on the carrier.

4. The process of claim 1, wherein the crystalline alumina silicate comprises dealuminated Y-zeolite with a unit cell size of between 24.30-24.40 Å.

5. The process of claim 1, wherein the carrier consists of between 30% and 70% by weight of the crystalline alumina silicate and between 30% and 70% by weight of alumina.

6. The process according to anyone of the preceding claims, wherein the feedstock is contacted with the catalyst at a space velocity of between 0.4 and 10 m^3 feedstock/m^3 catalyst/h.

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EUROPEAN SEARCH REPORT

Application Number
EP 96 10 1975

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	US-A-4 240 900 (EXXON) * column 4, line 12; claims 1-20 *	1,6	C10G45/54
Y		2	
X	EP-A-0 042 461 (EXXON) * page 6, line 19 - line 20; claims 1-11 *	1,3-6	
Y	EP-A-0 303 332 (SHELL OIL) * the whole document *	2	
A	EP-A-0 519 573 (SHELL) * page 2, column 5 - column 6; claims 1-23 *	1-6	
A	WO-A-94 26846 (AKZO NOBEL) * the whole document *	1-6	
A	FR-A-2 179 880 (BP) * the whole document *	1-6	

TECHNICAL FIELDS SEARCHED (Int.Cl.6)

C10G

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	28 May 1996	Michiels, P

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
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