

1

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PRODUCTION OF AVIATION GASOLINE

Wilhelmus M. J. Ruedisulj, The Hague, and Marius 't Hart, Amsterdam, Netherlands, assignors to Shell Oil Company, a corporation of Delaware

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This invention relates to the production of 100/130 grade aviation gasoline and to the aviation gasoline so produced.

An object of the invention is to provide a process for the production of 100/130 grade aviation gasoline which meets the specifications for such (MIL-F-5572A) and is less costly than when produced by previous methods involving reformed aviation base stocks.

Another object of the invention is to provide a novel aviation gasoline composition which meets the specifications for 100/130 grade and may be produced in larger quantities per given volume of alkylate.

The process of the invention broadly consists in the blending of certain known aviation gasoline constituents in new proportions with an aviation base stock prepared from a selected straight-run gasoline fraction through fractionation, platforming, reblending, and stabilization. The aviation gasoline broadly consist essentially of the specially prepared base stock in an amount upward of 30% by volume, alkylate in a substantial amount less than 50% by volume, minor amounts of isopentane or isopentane plus butane sufficient to satisfy the vapor pressure and volatility requirements, ethyl fluid and dye in an amount within the specification limits, and the remainder, if any, consisting of a heavy platformate fraction.

It is known that the octane number of straight-run gasolines and fractions thereof can be increased to an especially high degree in a practical operation by platforming them by which is understood a treatment thereof in the presence of added hydrogen and under suitable dehydrogenation conditions of temperature and pressure with an acidic platinum catalyst. The acidic platinum catalyst consists essentially of from 0.1 to 1% of platinum combined with an acidic support such as an alumina acidified by the inclusion of combined chlorine and/or fluorine or a cracking catalyst such as the proprietary silica-alumina, silica-magnesia, silica-zirconia, alumina-boria, etc., cracking catalysts. The particular advantage of platforming over the older so-called hydroforming with catalysts promoted with such materials as the oxides of molybdenum, chromium, cobalt, nickel, and tungsten, is that in the platforming process a definite and controlled amount of selective hydrocracking is effected and isomerization reactions are catalyzed to a much greater degree. The platforming operation is normally carried out under dehydrogenation conditions at temperatures between about 450° C. and 550° C. and under pressures between about 2 and 100 atmospheres.

Through the use of platforming as described, straight-run gasoline can be improved and improved in practical operation to an extent allowing use of the product as a component in premium grade motor gasoline. However, it has been determined that the components of straight-run gasoline boiling below about 85–95° C. are not materially improved by such treatment and it is the usual practice therefore to separate from the feed to the platforming operation the light components, i.e., those boil-

2

ing up to 85–95° C. and only platform the heavier part after which the light components which usually already have a fairly high octane number are combined with the platformate.

5 The products thus obtained, even when starting with a naphthenic gasoline, cannot however, not withstanding their high octane number generally be used as a component in the preparation of 100/130 grade aviation gasoline since when the said products are blended with the usual aviation gasoline components such as alkylate prepared from isobutane and butenes and/or pentenes, and isopentane, it is usually impossible to prepare mixtures which satisfy all the special and very strict requirements which are today made of such aviation gasoline, especially with respect to the volatility, heating value, stability and performance number (which is a measure of the take-off load) with the maximum lead content which is permissible according to the specifications.

It is, however, sometimes possible to prepare such mixtures when the platformate is derived from a naphthenic gasoline fraction boiling between approximately 85–95° C. and 130–140° C., provided the content of the said component in the mixture is kept to a relatively low value below about 30% by volume which means 20 that the mixture has a high alkylate content, viz. more than 50% by volume. This limitation with respect to the content of the platformate is, however, a drawback since this component is not only considerably cheaper than alkylate but is also more readily prepared starting 25 with initial materials which are much more available.

The invention now provides a process whereby 100/130 grade aviation gasoline may be prepared with platformate and with lesser quantities of alkylate thereby affording a lower cost per gallon of gasoline and a larger aviation gasoline production per given amount of alkylate.

The process according to the invention comprises separating a fraction boiling between approximately 65° C. and approximately 130–140° C. from a naphthenic straight-run gasoline, platforming this fraction under suitable conditions, combining the platformate so obtained 30 with the fraction boiling up to approximately 65° C. of the starting gasoline or with a part thereof, stabilizing the resultant mixture, and blending therewith the required amounts of alkylate, isopentane and/or butane, ethyl fluid and in some cases a small amount of heavy platformate. It is essential that a highly naphthenic straight-run gasoline containing upward of about 40% by weight of naphthenes be used as the starting material. Less naphthenic gasolines and especially natural gasolines are unsuited.

The platformate obtained as described has a higher octane number and performance number than those in which a gasoline fraction boiling between 85–95 and 130–140° C. derived from the same starting gasoline is used, but which is otherwise obtained in the same way, and can be mixed in quantities upward of 30% with the usual aviation gasoline components such as alkylate in an amount less than 50% and isopentane to form products which satisfy every requirement made of the aviation gasoline.

It is surprising that by increasing the boiling range of the straight-run material platformed to include that part which has hitherto been considered best omitted a greater proportion of the platformed base stock can be used with a reduced requirement for alkylate.

The platforming treatment is carried out in a manner known per se; however, under a narrower range of conditions viz. a pressure lower than 50 atmospheres preferably 2–30 atmospheres since with higher pressures, particularly when operating at temperatures higher than 500° C., the yield of liquid product is lower and moreover

the quality of the product as a aviation gasoline component declines. Temperatures lying between approximately 450 and 525° C. are used.

After separating the hydrogen gas phase which is produced in the platforming operation and which is recycled in the process, the liquid platformate obtained is combined with the components separated from the starting gasoline and boiling up to approximately 65° C. or with a part thereof. The pentane and lighter hydrocarbons in the mixture are then removed by stabilization. This is effected in a stabilization column in the manner used for stabilizing motor gasolines. The stabilized product thus obtained which is withdrawn from the bottom of the stabilizer forms the desired component from which by mixing with alkylate, isopentane, ethyl fluid, dye, and small amounts of any additional components, aviation gasoline of the required specification is prepared at a lower cost and greater yield per gallon of available alkylate.

It has been found to be also advantageous to use the above mentioned platformate product together with a low amount (in relation to this product) of the fraction of this product boiling above approximately 105° C. as a component in the aviation gasoline since by also using the said heavy fraction in a small quantity, which in connection with the volatility requirement of aviation gasoline should not generally exceed about 20% of the volume of the platformate product, it is possible to make a considerably further reduction in the content of alkylate in the aviation gasoline, e.g., to below 40%.

Example I

Starting from a Venezuelan gasoline having a naphthene content of 52% by weight and a final boiling point of 150° C. a fraction boiling between 65° C. and 135° C. was separated by fractional distillation in a quantity of 73.7% by weight. This fraction was platformed with commercial platforming catalyst at a through-put rate of 2.1 liters per liter of catalyst per hour together with hydrogen of 96% purity derived from the process in a quantity corresponding to 4.8 mols of hydrogen per mol of the gasoline fraction at approximately 490° C. and a pressure of approximately 30 atmospheres.

After separating the hydrogen-rich gas phase which was recycled, the liquid platformate which was obtained in a yield of 95% by weight, calculated on the gasoline fraction introduced, was combined with the components boiling below 65° C. which had been previously separated from the starting gasoline in a quantity of 17.3% by weight. The mixture was then freed in a stabilizing column of the pentane and lighter hydrocarbons still dissolved therein. The stabilized bottoms product withdrawn from the stabilizing column was obtained in a yield of 75.8% by weight based on the gasoline.

This product was combined with an alkylate prepared from isobutane and a mixture of butenes and pentenes and with isopentane and butane to form a mixture of the following composition in percentages by volume:

Stabilized produce	33.5
Alkylate	48.0
Isopentane	15.5
Butane	3.0

The mixture thus obtained had, after addition of 4 ml. of tetraethyl lead per U.S. gallon an F-4 performance number of 132.6 and in respect of all other properties satisfied the specification for aviation gasoline of 100/130 grade.

For the purpose of comparison it may be stated that when in separating the gasoline fraction to be reformed from the starting material the lower cutting temperature chosen was 85° C. instead of 65° C., other operating conditions remaining the same, a stabilized bottom product was obtained with which no mixture satisfying the specifications for 100/130 grade aviation gasoline could be prepared with the other component referred to above unless the content of stabilized bottom product was re-

duced to 27.5% by volume and the alkylate content was increased to 54% by volume.

This shows therefore that by operating according to the invention a considerable saving of alkylate can be effected.

Example II

A platformate-containing stabilized product was prepared in the same way as in Example I. A part of this product was separated by means of fractional distillation into a heavy fraction boiling above 105° C. and a lighter top product. A mixture was now prepared from the stabilized product and the heavy platformate fraction boiling above 105° C. which was separated therefrom together with the same alkylate as in Example I, isopentane, and butane, the composition of the mixture in percentages by volume being as follows:

Stabilized product	40.5
Heavy platformate fraction	6.0
Alkylate	38.2
Isopentane	12.3
Butane	3.0

After addition of 4 ml. of TEL per U.S. gallon this mixture had an F-4 performance number of 132.6 and in respect of all other properties it satisfied the specification for aviation gasoline of 100/130 grade.

A comparison of the composition of this mixture with that of the aviation gasoline referred to in Example I shows that the alkylate content of the final mixture can be reduced further by also adding a small percentage of the heavy platformate fraction.

We claim as our invention:

1. Aviation gasoline meeting the specification for 100/130 grade which consists essentially of alkylate in a substantial amount but less than 50% by volume, a minor amount of isopentane sufficient to meet the volatility requirements, tetraethyl lead in permissible amounts, and a depentanized catalytic reformat/straight-run stock obtained by (1) catalytically reforming a fraction of a straight-run gasoline containing at least 40% by weight naphthenes, said fraction having a lower cutting point of about 65° C. and an upper cutting point of about 130-140° C., by contacting it with an acidic platinum catalyst at a pressure between 2 and 30 atmospheres and a temperature between 450 and 525° C., (2) blending with the catalytic reformat the lower boiling material boiling up to about 65° C. separated from the said straight-run gasoline and (3) depentanizing the catalytic reformat/straight-run blend, said stock comprising at least 30% by volume of the gasoline, and any additional components in the gasoline being present in an amount less than 20% by volume of said stock.

2. An aviation gasoline according to claim 1 further characterized in containing a minor amount, less than 20% by volume of the depentanized catalytic reformat/straight-run stock, of a heavy reformat fraction prepared by removing from a portion of the catalytic reformat the material boiling up to about 105° C.

3. Process for the production of 100/130 grade aviation gasoline which comprises (1) separating from a naphthenic straight-run gasoline containing at least 40% by weight naphthenes by fractional distillation a light ends fraction boiling up to about 65° C. and a fraction having a lower cutting point of about 65° C. and an upper cutting point of about 130-140° C., (2) catalytically reforming the latter fraction by contacting it with an acidic platinum catalyst under a pressure between 2 and 30 atmospheres at a temperature between 450 and 525° C., (3) blending the catalytic reformat thus obtained with the said light ends fraction from the straight-run gasoline, (4) stabilizing the catalytic reformat/straight-run blend, and (5) blending the stabilized product thus obtained in an amount at least 30% by volume of the finished aviation gasoline with less than 50% by volume of alkylate, a minor amount of isopentane suffi-

5

cient to meet the volatility requirements and tetraethyl lead in permissible amounts, any additional components being present in an amount less than 20% by volume of the said stabilized product.

4. Process for the production of 100/130 grade aviation gasoline which comprises (1) separating from a naphthenic straight-run gasoline containing at least 40% by weight naphthenes by fractional distillation a light ends fraction boiling up to about 65° C. and a fraction having a lower cutting point of about 65° C. and an upper cutting point of about 130-140° C., (2) catalytically reforming the latter fraction by contacting it with an acidic platinum catalyst under a pressure between 2 and 30 atmospheres at a temperature between 450 and 525° C., (3) fractionating a part of the catalytic reformat thus obtained to separate a heavy fraction boiling above about 105° C., (4) blending the remainder of said catalytic reformat with at least part of said light ends fraction, (5) stabilizing the catalytic reformat/straight-run blend, (6) blending the stabilized product thus obtained in an amount at least 30% by volume of the finished gasoline with less than 20% by volume,

6

based on the stabilized product, of said heavy catalytic reformat, alkylate in an amount less than 50% by volume based on the gasoline, a minor amount of isopentane sufficient to meet the volatility requirements and tetraethyl lead in permissible amounts.

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