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PROCESS FOR PREPARING AVIATION BASE STOCK AND AVIATION GASOLINE

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This invention relates to aviation gasoline of 100/130 grade and to its production. It also relates to the production of aviation base stock, i. e., a special saturated hydrocarbon stock boiling within the aviation gasoline boiling range which may be combined in substantial amounts with the conventional aviation gasoline blending materials such as aromatic extracts, alkylate, isopentane, tetraethyl lead, etc. to given aviation gasoline meeting the specification of at least 100/130 grade. More particularly, it relates to an improvement in the use of catalytically reformed straight-run gasoline fractions in the production of improved aviation gasoline meeting the specifications for 100/130 grade.

An object of the invention is to provide a means whereby catalytically reformed straight-run fractions, other than aromatic concentrates, may be used in the production of aviation gasoline of at least 100/130 grade with low alkylate requirements.

It is known that the anti-knock properties of straight-run gasoline can be considerably increased by catalytically reforming them. The products obtained by catalytically reforming naphthenic gasoline are, however, generally unsuitable as a component in aviation gasoline since it is usually impossible to blend them in any appreciable concentration with alkylate, isopentane, butane, etc. to give a blend meeting the specifications for high grade aviation gasolines. It has been determined that, when catalytically reforming naphthenic straight-run gasolines, that part boiling below about 85–95° C. is not materially improved and it is the usual practice therefore to separate this light part boiling up to about 85–95° C. from the feed to the catalytic reforming operation. After reforming the heavier part, the light components, usually already have a fairly high octane number, are combined with the reformate. This product is also not generally suitable as a component in the preparation of 100/130 grade aviation gasoline since when it is blended with the usual aviation gasoline blending agents such as alkylate prepared from isobutanes and/or pentenes, and isopentane it is usually impossible to prepare mixtures which satisfy all of 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 practical blends meeting the specifications when the catalytically reformed stock is derived from a naphthenic gasoline fraction boiling between approximately 85–95° C. and 130–140° C. provided that the content of said component in the gasoline is kept to a relatively low value below about 30% by volume which means that the gasoline has a high alkylate content of more than 50% by volume. This limitation with respect to the content of the catalytically reformed product is, however, a drawback since this component is not only considerably cheaper than alkylate but is also more readily prepared starting with initial materials which are much more available.

It is also known that through the use of very narrow fractions of naphthenic straight-run gasolines products of upwards of 70% aromatics, e. g., so-called toluene concentrate, may be produced by catalytic treatment under the same conditions as used in catalytic reforming and that these aromatic concentrates are well suited for blending stocks for aviation gasoline when blended in small amounts with suitable aviation base stock, alkylate, isopentane, etc. Such aromatic concentrates may be used, however, in only relatively small amounts particularly in view of the volatility, heating value, and freezing point requirements. The present invention is not concerned with the production of such aromatic concentrates but with the production of suitable base stocks with which such aromatic concentrates, as well as the other usual aviation gasoline blending stocks, may be blended to produce specification gasoline.

The catalytic reforming of the relatively narrow fraction boiling between approximately 85–95° C. and 130–140° C. approaches the production of an aromatic concentrate. The so-called heavy reformate which is in fact an aromatic concentrate produced by catalytically reforming a narrow fraction under severe conditions to crack out most of the non-aromatic constituents or by catalytic reforming followed by fractionating out or extracting a highly aromatic concentrate, is not an aviation base stock but a blending component which may be added to a suitable aviation base stock only in very limited amounts. The unfractionated product from the catalytic reforming of an 85–95 to 130–140° C. fraction of naphthenic gasoline is borderline, i. e., it is between a true aromatic concentrate and a true aviation base stock. It may be used in some cases as an aviation base stock but only in quite small concentrations. To produce aviation gasoline of 100/130 grade with such material it is necessary to use large amounts of costly alkylate.

As shown in application Serial No. 543,271, filed October 27, 1955, it is possible by choosing a straight-run gasoline having at least 40% by weight of naphthenes to produce an aviation base stock superior to that obtained by catalytically reforming (platforming) a relatively narrow 85–95 to 130–140° C. fraction by platforming a broader fraction boiling between about 65° C. and 130–140° C. which fraction therefore includes part of the straight-run gasoline boiling below 85° C. which has hitherto been considered better left out. By platforming the 65° C. to 130–140° C. fraction, then blending the product with the unreformed part of the naphthenic gasoline boiling up to 65° C. and depentanizing the blend it is usually possible to produce aviation base stock which can be blended with the usual other aviation gasoline additives and/or blending agents to produce 100/130 grade gasoline with a lower concentration of costly alkylate. It is not, however, always possible to produce 100/130 grade aviation gasoline even in this

case with practical reforming severities without quite large concentrations of alkylate.

The present invention is based on the further discovery that the product obtained by catalytically reforming a 65 to 130–140° C. fraction, or for that matter also an 85 to 135–140° C. fraction, from a straight-run gasoline having at least 40% by weight naphthenes, followed by blending of the product with the fraction of the straight-run gasoline boiling below 65° C. and by stabilizing the resulting blend, may be further substantially improved as an aviation base stock for the production of 100/130 grade aviation gasoline by subjecting it either before or after the said blending and stabilizing to a fractional distillation to separate and remove therefrom that part of the reformate boiling between about 85° C. and 105° C.

It is of course, well known that for certain gasolines it is possible in some cases to improve the anti-knock properties of a gasoline somewhat by subjecting the gasoline to superfractionation to separate out low octane components. This is described, for example, in Patents Nos. U. S. 1,868,102 to Henderson et al., and U. S. 2,055,455 to Taylor et al.

This, however, requires an impractical fractionation in very costly fractionating equipment having the equivalent of many theoretical plates to separate out one or more fractions of very narrow boiling range. Fractionating to remove a relatively broad fraction boiling between 85–105° C. would not be expected to afford any appreciable improvement in the anti-knock properties of gasoline or of the aviation base stock boiling range fraction therefrom and for the usual run of gasolines no appreciable improvement is obtained in fact by such fractionation. This is illustrated in the following Examples I to III which are submitted for the sake of comparison.

Example I

Straight-run gasoline ex-Kirkuk crude was re-run to 140° C. end point. The F–1 clear octane number of this straight-run gasoline was 52.7 and with 1.5 ccs. TEL the F–1 octane number was 67.2. This straight-run material was fractionated in a fractionating column having 30 plates to separate an 85 to 105° C. fraction. The corresponding octane numbers of the separated fraction were 50.7 and 68.7 respectively. It is thus seen that in the case of straight-run gasoline the separation of the 85–105° C. fraction degrades rather than improves the gasoline.

Example II

Thermal gasoline produced by thermally cracking a mixture of East and West Texas crudes was re-run to 140° end point. The clear F–1 octane number of this product was 80.0 and with 1.5 ccs. TEL it was 86.9. This gasoline was then fractionated as before in the same fractionating column having 30 plates to separate the 85–105° C. fraction. The corresponding octane numbers of the separated fraction were 77.4 and 86.7, respectively. Here again with thermal gasoline the separation of the 85–105° C. fraction offers no improvement. The same situation exists for thermally reformed gasoline.

Example III

A catalytically cracked gasoline produced by catalytically cracking a Middle East crude was re-run to 140° C. end point. The F–1 clear octane number of this material was 89.7 and with 1.5 ccs. TEL it was 93.4. This material was fractionated as before in the same fractionating column to separate an 85–105° C. fraction. The corresponding octane numbers of the separated fraction were 87.8 and 94.3 respectively. Thus, in the case of catalytically cracked gasoline also the removal of the 85–105° C. fraction offers no improvement.

In the case of catalytically reformed gasoline of the same boiling range, and particularly one which has been

reformed with an acidic platinum catalyst, the separation of the 85–105° C. fraction, even in a relatively inefficient fractionating column having only 30 plates, affords a substantial improvement.

Example IV

A platformate from a commercial platforming operation had the following properties:

Gravity, API at 60° F	51.7
RVP	4.2
ASTM distillation—	
I. B. P. ° C	54
10% ° C	84
50% ° C	118
90% ° C	155
E. P. ° C	190
F–1 clear octane number	84.9
F–1+1.5 ccs. TEL	92.9
F–1+3.0 ccs. TEL	95.4

This platformate was fractionated in a 30 plate column to separate out a fraction boiling between 85° C. and 105° C. which fraction amounted to 20% by volume of the total. The F–1 clear octane number of this separated fraction was 65.3 and with 3 ccs. TEL it was 86.3. It is, thus, seen that in this case a sizeable improvement was obtained by removing this fraction.

Example V

Starting from a naphthenic gasoline a fraction boiling between approximately 65° C. and 135° C. was separated by fractional distillation in a quantity of approximately 74% by weight. This fraction which had a naphthenic content of 51% by weight was passed over a commercial platforming catalyst in four reactors connected in series at a rate of 2.1 liters per liter of catalyst per hour together with recycled gas containing 95% by volume of hydrogen (which was obtained from the process) in a quantity corresponding to 6.1 mols of hydrogen per mol of hydrocarbon and at a pressure of approximately 26 atmospheres. Heaters were interposed between the reactors in order to bring the vapor mixture flowing from one reactor to the next again to the desired reaction temperature. The vapor mixture was introduced in the first three reactors at a temperature of approximately 500 C. and in the fourth reactor at approximately 490° C. The vapor mixture flowing from the last reactor was led via a condenser to a separator in which the gas phase consisting of 95% by volume hydrogen was separated from the liquid reaction product. This liquid product, the yield of which was 95.5% by weight calculated on the gasoline fraction introduced, was now led into a stabilizing column together with the components of the starting gasoline which boiled below approximately 65° C. and which had been separated therefrom in a quantity of 10.7% by weight. Pentane and lighter hydrocarbons were separated in the stabilizing column and withdrawn from the top, the stabilized product being withdrawn as the bottom product. The F–4 performance number with 3 ccs. TEL per U. S. gallon of the stabilized product was 117.

The stabilized platformate thus obtained was then separated in a fractionating column with 30 trays into a fraction boiling above approximately 105° C. and a lighter top product which was then separated in a second fractionating column which also had 30 trays into a fraction boiling up to approximately 85° C. and an intermediate fraction boiling from approximately 85° C. to 105° C. The heavy and light fractions were combined and mixed 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.

Platformate	38
Alkylate	47
Isopentane	13
Butane	2

After addition of 3 ccs. TEL per U. S. gallon this product had an F–4 performance number of 131 while the percent by volume of the part volatilized at 105° C. was 52.5. It satisfied in every respect the specifications for an aviation gasoline of 100/130 grade.

When using the total platformate, i. e., without removing the fraction boiling between 85–105° C., it was not found possible to prepare a mixture which with 3 ccs. TEL per U. S. gallon satisfied the specifications of said aviation gasoline in respect of performance number and volatility.

In the process of the invention the fraction of the straight-run naphthenic gasoline reformed is essentially one derived from a straight-run gasoline having at least 40% by weight naphthenes and is preferably a fraction which boils between about 65° C. and 130–140° C. Some improvement may, however, also be obtained when starting with the more conventional fraction boiling between about 85° C. and 130–140° C., although the resultant product is inferior from that produced from the broader range material.

By catalytic reforming is meant a treatment in the vapor phase under dehydrogenation conditions at an elevated temperature between about 450° C. and 550° C. and under a pressure between about 2 and 100 atmospheres, preferably between 2 and 30 atmospheres, in the presence of hydrogen and a hydrogenation-dehydrogenation catalyst. Under these dehydrogenation conditions with naphthenic straight-run fractions there is an appreciable production of hydrogen which may be, and is preferably, cycled in part to the process. The catalytic reforming may be carried out in any one of the conventional manners of contacting the vapors with the catalyst and any of the conventional reforming catalysts which are essentially hydrogenation-dehydrogenation catalysts may be used. While many of the conventional reforming processes using, for example, chromium oxide, molybdenum oxide, tungsten sulfide may be used, the process of the invention is particularly adapted for platformed stocks, i. e., stocks catalytically reformed under the above conditions with an acidic platinum catalyst. The acidic platinum catalyst consists essentially of from .1 to 1% of platinum combined with an acidic support such as an alumina-containing combined chlorine and/or fluorine or a cracking catalyst such as the proprietory 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 oxides of molybdenum, chromium, cobalt, nickel, and tungsten is that in the platforming processes a definite and controlled amount of selective hydrocracking is effected and isomerization reactions are catalyzed to a much greater degree.

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 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 material which is then fractionated to remove the 85–105° C. fraction.

In separating the 85–105° C. fraction from the stabilized platformate the lower cut point may vary somewhat without affecting the results very much but the upper cut point of 105° C. is quite critical. The 85–105° C. fraction removed is a relatively broad range fraction and may be separated with ease in moderately efficient commercial fractionating equipment, for example a fractionating column containing only 30 plates. This is in sharp contrast to the impractical super fractionation required to separate out the very narrow boiling fractions of low octane components from straight-run gasoline, thermally reformed gasoline, thermally cracked gasoline, and catalytically cracked gasoline.

The fractionation to separate the 85–105° C. fraction may be effected on the stabilized product as described or it may be carried out on the platformate prior to blending the lower boiling straight-run material (boiling up to about 65° C.) and stabilizing.

Any of the alkylates commercially used in preparing 100/130 grade aviation gasoline blends may be used. These alkylates are prepared by alkylating isobutane and/or isopentane with propylene and/or butylenes and/or amylenes using either sulfuric acid or hydrofluoric acid catalysts. The preferred alkylate is prepared from isobutane or butylenes.

The isopentane used in preparing the aviation gasoline blend is normally the so-called technical grade such as commonly used for this purpose.

It is to be understood that in preparing the aviation gasoline blend small amounts of highly aromatic materials, tetraethyl lead fluid, dyes, corrosion inhibitors, etc. may be added in accordance with the specification for 100/130 grade aviation gasoline which specification is designated MIL–F–5572A. Such additional materials are, however, used in only small amounts and are present in the finished gasoline in amounts less than 10% by volume.

I claim as my invention:

1. Process for the production of 100/130 grade aviation gasoline which comprises 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 an initial boiling point of about 65° C. and a final boiling point between 130° C. and 140° C., catalytically reforming the latter fraction, blending the reformate thus produced with said light ends fraction and stabilizing the blend, fractionally distilling the stabilized blend to separate and remove therefrom the material boiling between about 85° C. and 105° C., and blending the remainder in an amount at least 30% by volume with alkylate in an amount less than 50% by volume and isopentane in an amount sufficient to meet the volatility requirements, any additional components being present in amounts less than 10% by volume of the finished gasoline.

2. Process according to claim 1 further characterized in that the fractionation to separate the 85–105° C. fraction is effected on the catalytic reformate prior to blending with the said light ends fraction and stabilizing.

3. Process for the production of 100/130 aviation grade gasoline which comprises 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 an initial boiling point of about 65° C. and a final boiling point between 130 and 140° C., catalytically reforming the latter fraction with a platinum catalyst under a pressure between 2 and 30 atmospheres and a temperature between 450 and 550° C., blending the catalytic reformate thus produced with said light ends fraction and stabilizing the blend, fractionally distilling the stabilized blend to separate and remove therefrom material boiling between about 85° C. and 105° C., and blending the remainder in an amount at least 30% by volume with alkylate in an amount less than 50% by volume and isopentane in an amount sufficient to meet the volatility requirements, any

additional components being present in amounts less than 10% by volume of the finished gasoline.

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