

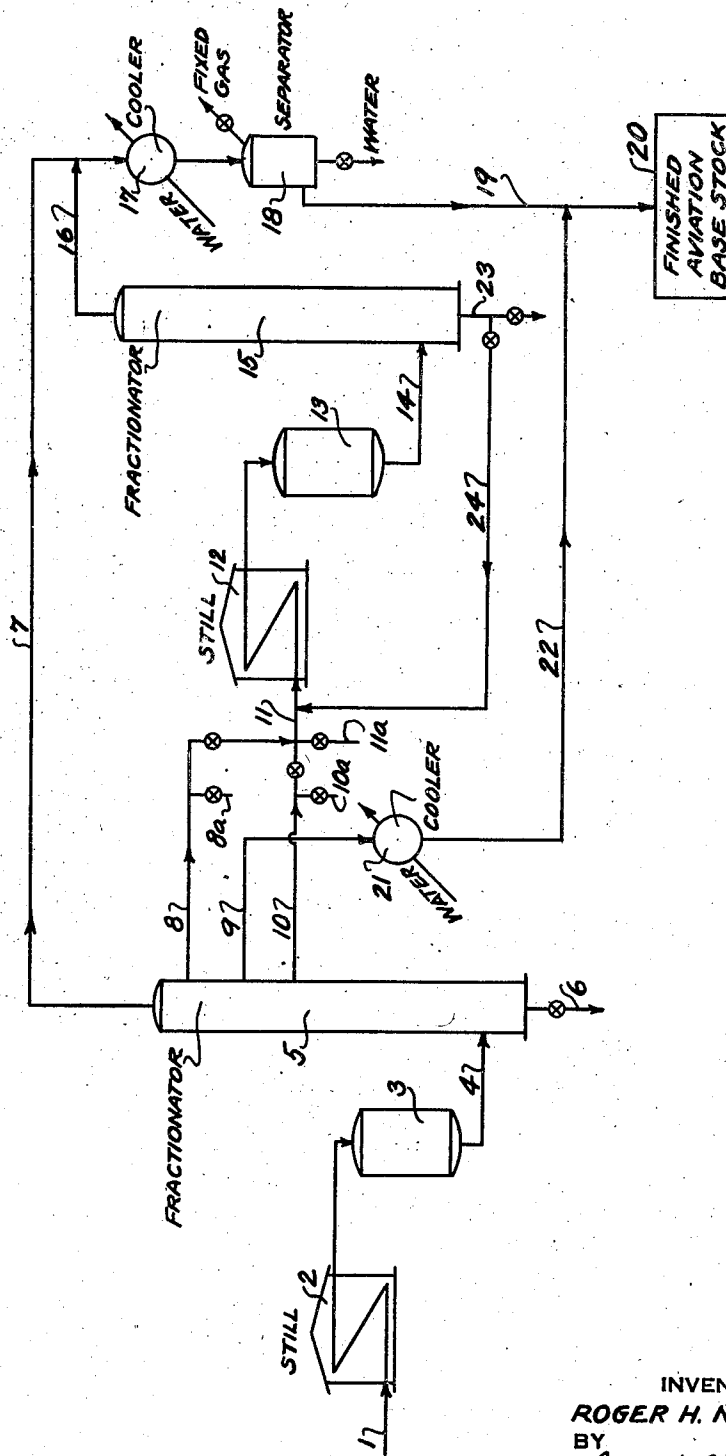
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PRODUCTION OF AVIATION GASOLINE

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## UNITED STATES PATENT OFFICE

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## PRODUCTION OF AVIATION GASOLINE

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This invention relates to the production of desirable motor fuels and especially base material for use in aviation engines including fighting grade as well as training and commercial grades of aviation gasoline.

One object of the invention is to produce a maximum quantity of aviation gasoline of superior quality from hydrocarbons higher boiling than the desired product. Another object is to minimize and simplify the treatment of cracked material in the production of acceptable aviation base material. Other objects will be apparent from the detailed description which follows.

In practicing the invention cracked hydrocarbons (preferably from a catalytic cracking operation utilizing high activity catalysts of the general type of silica-alumina from naturally occurring clays or synthetically produced) are fractionated into at least four cuts, namely a first or overhead fraction boiling to about 180° F., a second fraction in the boiling range of about 180 to about 250° F., a third fraction in the boiling range of about 250 to 325° F., and a fourth fraction in the boiling range of about 325 to 500° F. The first cut is predominantly paraffins with some undesirable olefins, the second cut is high in undesirable naphthenic constituents, and the third and fourth cuts are essentially aromatics. If the fresh charge or original stock to be cracked is a naphtha or gas oil, the only cut of the first three which actually requires any subsequent treatment is the second or 180 to 250° F. cut. To raise this cut to acceptable quality a severe vapor phase treatment with high activity cracking catalyst is required. If the fresh charge or original cracking stock is heavier than gas oil, the first (initial to 180° F.) cut requires some light or moderate treatment to remove or to convert olefins in addition to the severe or drastic treatment of the second or intermediate 180–250° F. cut. Of course, to further increase the yield of aviation gasoline the fourth or 325–500° F. cut should be re-cracked. Since this material is more refractory than the fresh charge it requires the severe or drastic cracking conditions of the second or 180 to 250° F. cut and may advantageously be combined with the latter. Recycling may be utilized in this severe treating stage to insure a maximum yield of aviation gasoline.

In order to illustrate this invention and the manner of its use one concrete embodiment of apparatus adapted to practice of the invention is indicated diagrammatically in the single figure of the accompanying drawing.

The charging stock, which may consist of crude

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hydrocarbons higher boiling than aviation gasoline, is charged by line 1 to still 2 where the charge is vaporized and sent under cracking conditions to and through a reactor 3, which may be of any suitable or desired type, but is preferably a catalytic reactor of the fluid, static or moving bed type charged with any known or suitable cracking catalysts. The products of the cracking reaction are passed by line 4 to a fractionating column 5 wherein the products are divided into at least four cuts in addition to a bottom cut which may be withdrawn from fractionator 5 by line 6. The four cuts comprise, first, an overhead cut containing the fixed gases and other products in vapor form having an end point of approximately 180° F., which leaves fractionator 5 by line 7; second, a side stream liquid fraction in the boiling range of approximately 180° to 250° F. leaving fractionator 5 by line 8; third, a higher boiling liquid fraction in the boiling range of approximately 250 to 325° F., leaving fractionator 5 by line 9; and fourth, a liquid fraction in the boiling range of approximately 325° to 500° F. leaving fractionator 5 by line 10. By preference the second cut (180°–250° F.) and the fourth cut (boiling range 325–500° F.) are combined and sent by line 11 to a vaporizing element or still 12 and thence into a reactor 13 where they are subjected to drastic cracking conditions over high activity cracking catalysts, the products leaving reactor 13 by line 14, which sends the same into a fractionating column 15. An overhead fraction, cut to the end point of the desired aviation gasoline (as to 325° F.), passed by line 16 from fractionator 15 and, augmented by the first cut from fractionator 5 through the joining of line 7 to line 16, passes through condenser 17 and separator 18 and thence by line 19 to storage at 20. The third cut, leaving fractionator 5, by line 9 passes through cooler 21 and thence by line 22 to aviation base storage 20.

Lines 8 and 10 for the second and fourth cuts from fractionator 5 each have draw-off lines 8a and 10a, respectively, by which some or all of either of the cuts may be withdrawn before reaching line 11, which leads to vaporizing still 12. Any material, in the boiling range of the second and fourth cuts, which is similar to these cuts or which will be advantageously affected by the severe conditions in catalytic reactor 13 to produce additional quantities of aviation gasoline of high quality may be fed by line 11a into line 11. Any desired amount of bottoms from fractionating tower 15, leaving the latter by line 23, may be repassed or recycled through the drastic catalytic

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treating stage as by line 24, which joins line 11 in advance of the vaporizing still 12.

In general, the operating conditions for the first cracking zone (reactor 3) are as follows:

For naphthas and gas oils:

Temperature in the range of 750 to 850° F.

Feed rates .75:1 to 2:1 (volume of charge liquid basis per hour per volume of catalyst).

Catalyst activity 38 to 46% (indicates percentage of a standard fuel as East Texas gas oil which is converted by the catalyst under standard operating conditions into 410° F. end point gasoline).

Pressures up to 75 lbs. per square inch gauge, pressure used depending on catalyst activity, the higher the catalyst activity the lower the pressure employed.

For heavy stocks:

Temperature in the range of 800 to 900° F.

Feed rates .75:1 to 1.5:1.

Catalyst activity 30 to 40%.

Low pressures—up to 35 lbs. per square inch gauge.

Vaporizing fluid—as steam up to 20% by weight of charge.

For the second zone (reactor 13) the operating conditions are as follows:

Temperature in the range of 800 to 925° F.

Feed rates .5:1 to 1:1.

Catalyst activity 40% or above.

Pressure in the range of 35 to 100 lbs. per square inch gauge.

In general, the operating conditions in this zone are not less severe than those in the first cracking zone; for example, if temperatures, feed rates and pressure are the same, then the catalyst in the second zone must have higher activity to produce the desired results. When utilizing line 24 to recycle higher boiling products in the second zone the ratio of recycle to feed to the zone may range up to 2:1 but the overall rate of feed to the zone should not exceed 1½:1.

The operation indicated in the drawing can be utilized as shown when the original charging stock to still 2 is a naphtha or a gas oil. When high boiling distillates or residual crude materials are utilized as the original charging stock resulting in the production of an undue amount of olefins, some supplemental treatment of at least the first cut of line 7 (initial to 180° F.) and sometimes of the third cut of line 9 (250°–325° F.), is required, such treatment (not illustrated) being to remove or to convert the olefins into more stable hydrocarbons. There is a considerable choice of treatment for this purpose, such as: light sulphuric acid treat; liquid phase polymerization of the general type disclosed in United States Patent 2,273,038, issued February 17, 1942, to E. J. Houdry and J. P. Daugherty, Jr.; or vapor phase catalytic treatment generally similar to that effected in the second zone (reactor 13) but under mild conditions, the operation being conducted primarily to reduce acid heat after the manner disclosed in the copending application of A. G. Peterkin, Serial No. 385,465, filed March 27, 1941, which issued as Patent No. 2,347,216 on April 25, 1944, and which describes on page 2 of the printed patent the method for determining the activity (or activity index) of catalysts.

It is to be understood that only the most essential pieces of equipment are indicated in the drawing and then only diagrammatically; aux-

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iliary equipment such as pumps, heat exchangers, regenerating circuits, etc., are omitted since they are not necessary to an understanding of the invention. When static bed reactors are used in the catalytic zones at 3 and 13, a sufficient number of them may be provided to permit continuous operation.

High activity catalysts can be produced from naturally occurring silica-alumina or clay deposits by suitable chemical or other treatment and can be utilized advantageously in both catalytic zones 3 and 13. However, it is preferable to use silica-alumina catalysts produced synthetically, as for example in accordance with the disclosure of United States Patents 2,283,172 and 2,283,173, issued to J. R. Bates on May 19, 1942, because synthetic catalysts give higher octanes to the hydrocarbons than do the catalysts produced from clay. Cracking catalysts other than silica-alumina, which may be utilized in accordance with the present invention, are highly active compounds of the following: silica-zirconia, silica-alumina-zirconia, silica-alumina-beryllia, etc. As indicated above, the operating conditions in catalytic zone 13 should be more severe or drastic than those utilized in zone 3, for the reason that the charging stock to the latter zone is fresh crude rather than cracked products as to zone 13. Best results are secured in zone 13 when synthetic catalysts of high activity and purity (of at least 40% activity) are utilized under adequately severe conditions of temperature, feed rate and pressure.

Equipment to stabilize the aviation base stock leaving separator 18 may be provided, if needed, for the finished aviation base stock, but illustration of it has been omitted from the drawing since a showing of it is not necessary to the understanding of the invention. The following examples give results that are typical of operations in accordance with the invention.

#### Example 1

Fresh East Texas gas oil of 36° A. P. I. gravity and 440–720° F. boiling range was subjected to cracking in the first zone over 45 activity index synthetic silica-alumina cracking catalyst maintained at an average temperature of 800° F. and under ten pounds gauge pressure at 1:1 feed rate (liquid volume of charge per hour per volume of catalyst) for 10 minute on-stream operating periods. The products of the first zone were subjected to fractionation and division into cuts after the manner indicated in the drawing. For purposes of subsequent comparison the yield of aviation gasoline (275° F. at 90% evaporation and 7 lbs. Reid vapor pressure) from this first cracking stage was obtained and found to be 32.3% by volume of the charge. It had the following characteristics: acid heat—35; 1C octane with 4 cc. tetraethyl lead—94.0; 3C rating with 4 cc. lead—94% S in M.

The second cut (approximately 180 to 250° F.) alone was charged to and subjected to treatment in the second zone (reactor 13) over 45 activity index synthetic silica-alumina catalyst maintained at an average temperature of 830° F. and under 50 lbs. gauge pressure at .75:1 feed rate for 10 minute on-stream operating periods. Adding the resulting aviation gasoline to the first cut (initial to 180° F.) and to the third cut (250 to 325° F.) gave a yield after removal of excess isopentane of aviation gasoline (275° F. at 90% evaporation at 7 lbs. Reid vapor pressure) of 27%

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by volume of the original charge having the following characteristics:

Acid heat=25

1C octane with 4 cc. tetraethyl lead=99.8

3C rating with 4 cc. tetraethyl lead=99.7% S in M

As compared with the aviation gasoline from the first cracking step this treatment of the second cut alone gave a volumetric loss of yield of slightly over 5% but produced a marked improvement in quality.

Treating both the second cut (180–250° F.) and the fourth cut (325–500° F.) together in the second cracking zone (reactor 13) under the operating conditions stated in the preceding paragraph and combining the resulting aviation gasoline with the first cut (initial to 180° F.) gave, after removal of excess iso-pentane, a yield of aviation gasoline (275° F. at 90% evaporate) and 7 lbs. Reid vapor pressure of 31.6% by volume of the original charge having the following characteristics:

Acid heat=25

1C octane with 4 cc. tetraethyl lead=99.4

3C rating with 4 cc. tetraethyl lead=S+0.3

By recycling in the second cracking zone the 325 to 450° F. cut of products from the same zone in the ratio of 1:1 (one volume of recycle to one volume of charge to the zone) under the same operating conditions for this second zone as previously indicated in this Example 1 except that the total feed rate due to the recycling became 1½:1 instead of .75:1, the overall yield of aviation gasoline (275° F. at 90% evaporate at 7 lbs. Reid vapor pressure) was raised to 34.5% by volume of the original charge, with the following characteristics:

Acid heat=25

1C octane with 4 cc. tetraethyl lead=100

3C rating with 4 cc. tetraethyl lead=S+0.7

#### Example 2

A cut of East Texas crude boiling between 440 and 970° F. was subjected to cracking in the first zone over 36 activity index synthetic silica-alumina cracking catalyst maintained at an average temperature of 850° F. and under 10 lbs. gauge pressure with 10% of steam by weight and at a feed rate of 1:1 for 10 minute on-stream periods. The material in the product boiling in the aviation boiling range after removal of excess iso-pentane was 28.1% by volume of fuel (275° F. at 90% evaporate and 7 lbs. R. V. P.) having the following characteristics: acid heat=100; 1C octane+4 cc. T. E. L.=91. The 3C rating was not obtained because the acid heat and gum were too high for satisfactory aviation fuel.

Fractionation of the products was effected as illustrated in the drawing. The second and fourth cuts were combined and treated in the second zone (reactor 13) with recycling of all products boiling above 325° F. under operating conditions as follows: average catalyst temperature 850° F., synthetic silica alumina cracking catalyst of 40 activity index, feed rate .75:1 fresh feed or 1½:1 total feed, pressure 50 lbs. per sq. in. gauge, no steam, for ten minute on-stream periods. The products boiling below 325° F. were combined with the third cut from the first zone and with the first cut from the first zone after this latter cut had been treated with 10 lbs. of sulphuric acid per barrel to remove olefins. After removal of excess iso-pentane the yield of

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aviation gasoline (275° F. at 90% evaporate and 7 lbs. R. V. P.) was 30.1% by volume and its characteristics were:

Acid heat=25

1C octane with 4 cc. T. E. L.=99.3

3C rating with 4 cc. T. E. L.=S+.7

With naphtha charging stocks the charging rate to the first cracking zone is usually higher than for the gas oil charge of Example 1 but the processing conditions and qualities of product are about the same as in Example 1. The yield of aviation gasoline from the first cracking zone is somewhat higher, however, as of the order of 20% higher, the increase holding substantially uniformly through the treatments in the second cracking zone.

I claim as my invention:

1. In the production of high quality motor fuels including aviation gasoline and aviation base stock the process which comprises dividing the synthetic crude from a cracking operation into at least four cuts substantially as follows: initial –180° F., 180–250° F., 250–325° F. and 325 to 500° F., subjecting the second and the fourth of said cuts to the action of high activity cracking catalysts under severe cracking conditions, and combining the products from said catalytic operation in the boiling range of aviation gasoline with the first and third of said cuts to make a superior aviation base stock.

2. In the production of high quality motor fuels including aviation gasoline and aviation base stock the process which comprises dividing the synthetic crude from a cracking operation into at least four cuts substantially as follows: initial –180° F., 180–250° F., 250–325° F. and 325 to 500° F.; subjecting the second and the fourth of said cuts to the action of high activity cracking catalysts under severe cracking conditions, recycling in said catalytic operation at least a part of the products higher boiling than aviation gasoline, and combining the products from said catalytic operation in the boiling range of aviation gasoline with the first and third of said cuts to make a superior aviation base stock.

3. In the production of high quality motor fuels including aviation gasoline and aviation base stock the process which comprises dividing the synthetic crude from a cracking operation into at least four cuts substantially as follows: initial –180° F., 180–250° F., 250–325° F. and 325 to 500° F.; treating said first and third cuts to reduce its content of olefins, subjecting the second and the fourth of said cuts to the action of high activity cracking catalysts under severe cracking conditions, and combining the resulting products in the aviation boiling range from all said cuts to provide a superior aviation base stock.

4. In the production of high quality motor fuels including aviation gasoline and aviation base stock the process which comprises dividing the synthetic crude from a cracking operation into at least four cuts substantially as follows: initial –180° F., 180–250° F., 250–325° F. and 325–500° F., treating said first cut to reduce its content of olefins, subjecting the second and the fourth of said cuts to the action of high activity cracking catalysts under severe cracking conditions, recycling in said catalytic operation at least a part of the products higher boiling than aviation gasoline, and combining the resulting products in the aviation boiling range from all said cuts to provide a superior aviation base stock.

5. In the production of high quality motor fuels

including aviation gasoline and aviation base stock the process which comprises converting crude hydrocarbons higher boiling than aviation gasoline into lighter products over active cracking catalyst maintained in the temperature range of 750 to 900° F. at pressure below 75 lbs. per square inch and at charging rates in the range of .75 to 1 to 2:1 (liquid volume of charge per volume of catalyst per hour), dividing the resulting products into at least three cuts substantially as follows: initial -180° F., 180-250° F., and 250-325° F.; subjecting the second of said cuts to a second catalytic operation over high activity cracking catalyst under operating conditions at least as severe as for said converting operation; and combining the products from said second catalytic operation in the boiling range of aviation gasoline with the first and third of said cuts to make a superior aviation base stock.

6. In the production of high quality motor fuels including aviation gasoline and aviation base stock the process which comprises converting crude hydrocarbons higher boiling than aviation gasoline into lighter products over active cracking catalyst maintained in the temperature range of 750 to 900° F. at pressure below 75 lbs. per square inch and at charging rates in the range of .75 to 1 to 2:1 (liquid volume of charge per volume of catalyst per hour), dividing the resulting products into at least four cuts substantially as follows: initial -180° F., 180-250° F., 250-325° F., and 325-500° F.; subjecting the second and fourth of said cuts to a second catalytic operation over high activity cracking catalyst under operating conditions at least as severe as for said converting operation; and combining the products from said second catalytic operation in the boiling range of aviation gasoline with the first and third of said cuts to make a superior aviation base stock.

7. In the production of high quality motor fuels including aviation gasoline and aviation base stock the process which comprises converting crude hydrocarbons higher boiling than aviation gasoline into lighter products over active cracking catalyst maintained in the temperature range of 750 to 900° F. at pressure below 75 lbs. per square inch and at charging rates in the range of .75 to 1 to 2:1 (liquid volume of charge per volume of catalyst per hour), dividing the resulting products into at least three cuts substantially as follows: initial -180° F., 180-250° F., and 250-325° F.; subjecting the second of said cuts to a second catalytic operation over high activity cracking catalyst under severe cracking conditions including temperature in the range of 800 to 925° F., feed rates of 1/2:1 to 1:1, and combining the products from said second catalytic operation in the boiling range of aviation gasoline with the first and third of said cuts to make a superior aviation base stock.

8. In the production of high quality motor fuels including aviation gasoline and aviation base stock the process which comprises converting crude hydrocarbons higher boiling than aviation gasoline into lighter products over active cracking catalyst maintained in the temperature range of 750 to 900° F. at pressure below 75 lbs. per square inch and at charging rates in the range of .75 to 1 to 2:1 (liquid volume of charge per volume of catalyst per hour), dividing the result-

ing products into at least four cuts substantially as follows: initial -180° F., 180-250° F., 250-325° F., and 325-500° F.; subjecting the second and fourth of said cuts to a second catalytic operation over high activity cracking catalyst under severe cracking conditions including temperature in the range of 800 to 925° F., feed rates of 1/2:1 to 1:1, and combining the products from said second catalytic operation in the boiling range of aviation gasoline with the first and third of said cuts to make a superior aviation base stock.

9. In the production of high quality motor fuels including aviation base stock the process which comprises converting hydrocarbons in the naphtha and gas oil boiling ranges by subjecting them in the temperature range of 750 to 850° F. at pressures not exceeding 75 lbs. per sq. in. gauge and at feed rates in the range of .75:1 to 2:1 (liquid volume of charge per hour per volume of catalyst) to the action of cracking catalyst of at least 38 activity index, dividing the resulting products into at least four cuts substantially as follows: initial -180° F., 180 to 250° F., 250-325° F. and 325-500° F., subjecting the second and fourth of said cuts to a second catalytic operation over cracking catalyst of at least 40 activity index under conditions of temperature in the range of 800 to 925° F., feed rate in the range of .5:1 to 1:1 and pressure not exceeding 100 lbs. per sq. in. gauge more severe than in said converting operation, recycling products higher boiling than aviation gasoline in said second catalytic operation in a ratio to the feed thereto not exceeding 2:1 but giving an overall feed rate to said second operation not exceeding 1 1/2:1, and combining the products in the boiling range of aviation gasoline from said second catalytic operation with the first and third of said cuts to make a superior aviation base stock.

10. In the production of high quality motor fuels including aviation base stock the process which comprises converting heavy hydrocarbons by subjecting them in the temperature range of 800 to 900° F. at pressure not exceeding 35 lbs. per sq. in. gauge at feed rates in the range of .75:1 to 1.5:1 (liquid volume of charge per hour per volume of catalyst) and with up to 20% by weight vaporizing fluid to the action of a cracking catalyst having an activity index of at least 30, dividing the resulting products into at least four cuts substantially as follows: initial -180° F., 180-250° F., 250-325° F., and 325-500° F., treating the first cut to reduce its content of undesirable olefins, subjecting the second and fourth of said cuts to a second catalytic operation over cracking catalyst of at least 40 activity index under conditions of temperature in the range of 800 to 925° F., feed rate in the range of .5:1 to 1:1 and pressure not exceeding 100 lbs. per square inch gauge more severe than in said converting operation, recycling products higher boiling than aviation gasoline in said second catalytic operation in a ratio to the feed thereto not exceeding 2:1 but giving an overall feed rate to said second operation not exceeding 1 1/2:1, and combining the products in the boiling range of aviation gasoline from said second catalytic operation with said treated first cut and with said third cut to make a superior aviation base stock.