PRODUCTION OF AVIATION GASOLINE

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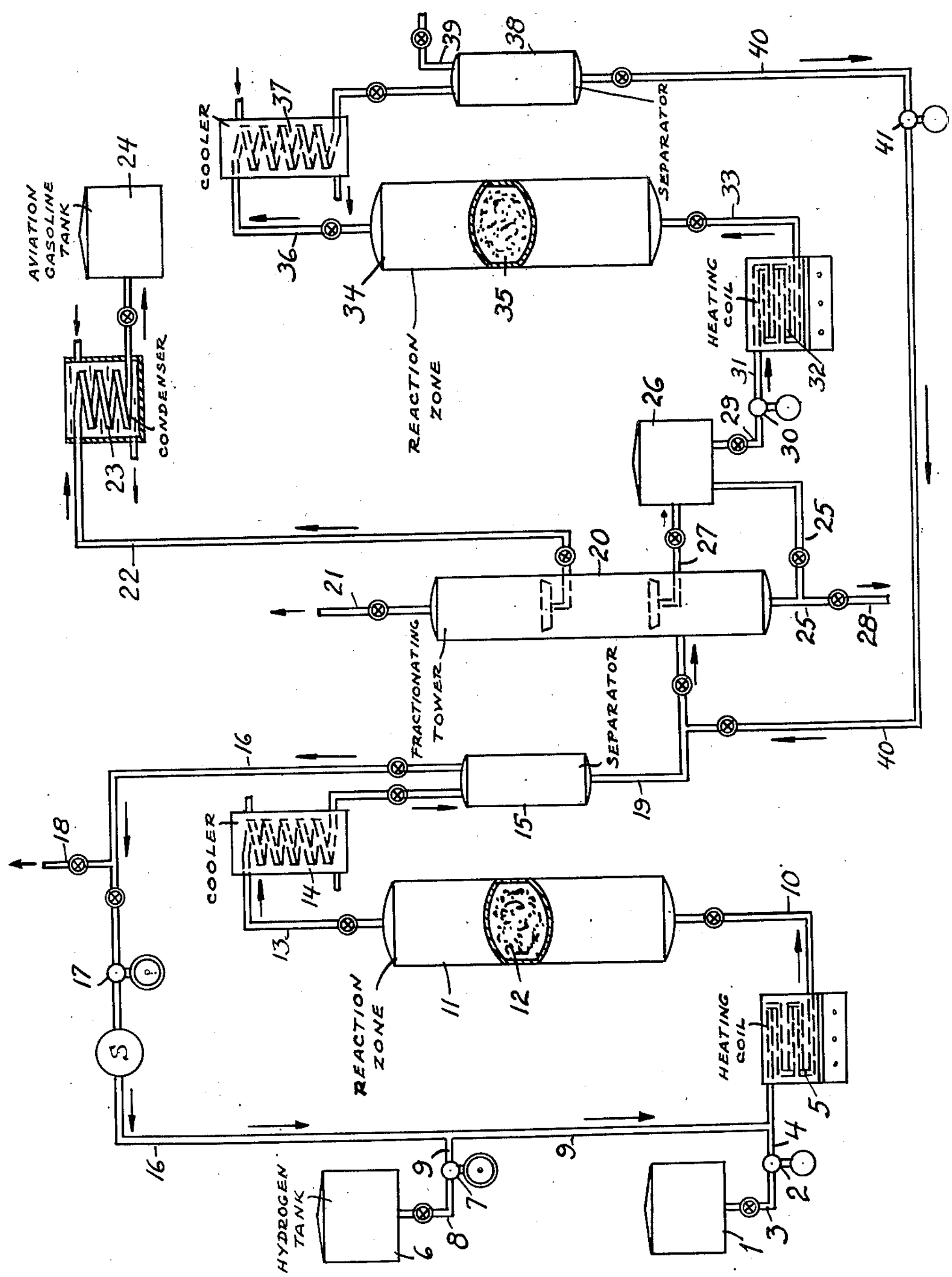

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PRODUCTION OF AVIATION GASOLINE

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This invention relates to the production of aviation gasoline of high octane number and other desirable characteristics and is more particularly concerned with an improved process by means of which the yield of aviation gasoline obtained from a given hydrocarbon oil may be substantially increased.

It is known that aviation gasoline of high octane number may be produced from hydrocarbon oils of the type of naphthas, heavy naphthas and kerosenes by subjecting such oil to catalytic reforming preferably in the presence of hydrogen and segregating from the products of reforming a fraction boiling in the range of an aviation gasoline, say from 100 to 300° F. The principal reactions which occur in the catalytic reforming are aromatization and dehydrogenation. Relatively little cracking occurs because it is found that the catalysts and operating conditions which are most favorable for aromatization and dehydrogenation do not permit extensive cracking.

In catalytic reforming processes of the type referred to, an appreciable proportion of the liquid products comprises aromatic hydrocarbons which boil well above the range of aviation gasoline. These hydrocarbons except for their high boiling point would otherwise be admirably adapted for use in aviation gasoline. Nothing would be gained by recycling them through the catalytic reforming process because the conditions prevailing therein are not conducive to cracking to produce hydrocarbons of lower boiling range. Hence the higher boiling fractions of the reformed product represent a direct loss insofar as the desired aviation gasoline is concerned.

Highly aromatic fractions are normally very refractory and are not especially suited to cracking without a preliminary hydrogenation treatment. Notwithstanding this fact, I have now found that the higher boiling fractions of the reformed product, that is, those boiling above about 300° F., may be converted to a substantial extent into lower boiling aromatic hydrocarbons boiling within the range of aviation gasoline by a process of catalytic cracking.

The present invention therefore has as its principal object the provision of a process whereby a hydrocarbon oil of the type of naphtha, heavy naphtha or kerosene is subjected to catalytic reforming in the presence of hydrogen, the liquid products of reforming are separated into a fraction boiling in the range of aviation gasoline and a fraction boiling above said range, the latter fraction is subjected to catalytic cracking whereby additional hydrocarbons boiling in the aviation gasoline range are obtained and the two fractions boiling in said range are combined with the result that a substantially larger yield of high octane number aviation gasoline is obtained from the initial oil than would be the case if the higher boiling fractions of the reformed product were discarded.

The manner in which the process may be carried out will be fully understood from the following description when read with reference to the accompanying drawing which is a semi-diagrammatic view in sectional elevation of one type of apparatus suitable for the purpose.

Referring to the drawing, numeral 1 designates a supply of a hydrocarbon oil such as a virgin heavy naphtha. Pump 2 withdraws oil from tank 1 through line 3 and forces it through line 4 into a heating means 5 wherein it is heated to a temperature sufficient to maintain the desired temperature in the reaction zone into which it is presently to be introduced. Numeral 6 designates a supply of hydrogen or a gas rich in free hydrogen. Compressor 7 withdraws hydrogen from tank 6 through line 8 and forces it through line 9 which meets line 4 so that a mixture of hydrogen and oil flows through the heating means 5. It will be understood that the oil and hydrogen may be heated in separate heating means, if desired. The heated mixture of oil and hydrogen flows through line 10 into a reaction zone 11 which contains a catalytic material 12, the nature of which will be described below.

Reaction zone 11 is maintained under conditions which promote catalytic reforming in the presence of hydrogen, chiefly aromatization and dehydrogenation. Temperature is maintained between 850 and 1050° F. and pressure between slightly above atmospheric and about 500 pounds per square inch. The oil is passed through reaction zone 11 at a rate between 0.3 and 3.0 volumes of liquid oil per volume of catalyst per hour and the quantity of gas rich in free hydrogen which accompanies the oil is between 1000 and 5000 cubic feet per barrel of oil. This gas should contain between 30 and 90 mol percent of free hydrogen and it will be understood that the larger volumes of gas are used with the lower concentrations of hydrogen therein and vice vesa. The catalyst 12 in reaction zone 11 is one which promotes aromatization and dehydrogenation and may be selected from a variety of different materials. Especially suitable catalysts for this purpose comprise a major proportion of aluminum oxide in any of its various forms and a minor proportion, say from about 1 to 40% by weight of an oxide or sulfide of a metal of the IV, V, VI or VIII groups of the periodic system. As examples of this type of catalyst may be mentioned alumina, alumina gel, peptized alumina gel, aluminum hydrate, peptized aluminum hydrate, and activated alumina upon which is deposited or with which is incorporated from 1 to 20% by weight of the oxides of molybdenum, chromium, tungsten, vanadium, cobalt or nickel. The reforming reaction in reaction zone 11 is conducted under conditions and for a time such that there will be no net consumption of free hydrogen and preferably so that there will be a net production of free hydrogen. For this reason, it is unnecessary continuously to supply hydrogen from an extraneous source because the hydrogen produced in the reforming reaction may be continuously recycled.

Products of reaction leave reaction zone 11 through line 13, pass through a cooling means 14 and are collected in a separating means 15 wherein liquids and gases may be separated. The gaseous products which will consist primarily of hydrogen together with small amounts of low molecular weight hydrocarbons such as methane, ethane and propane are removed from separating means 15 through line 16 and are returned to line 9 by means of booster compressor 17 for recycling through the reaction zone. Excess gas may be vented if necessary through line 18. A scrubbing means denoted by the letter S may be placed in line 16 to remove at least a portion of the hydrocarbon constituents from the gases before the latter are recycled. This scrubbing means may comprise, for example, a tower in which the gases are caused to rise upwardly in countercurrent to a downwardly flowing stream of a hydrocarbon oil capable of absorbing hydrocarbons under conditions at which it absorbs little or no hydrogen. Other methods of separating hydrocarbons from hydrogren may of course be used.

Liquid products of reaction are removed from separating means 15 through line 19 and introduced into a fractionating means 20. Normally gaseous hydrocarbons and hydrocarbons too volatile for incorporation in aviation gasoline are removed from fractionating means 20 through line 21. An aviation gasoline fraction is removed from the fractionating means through line 22 and after passing through a cooling and condensing means 23 is collected in a tank 24. Fractions boiling above the range of aviation gasoline, say above about 300° F., are removed from the fractionating means 20 through line 25 and collected in a tank 26. In some cases where there is a large proportion of higher boiling fractions present, say fractions boiling above about 360° F., it may be desirable to remove a fraction boiling between 300 and 360–380° F. through line 27 and collect it in tank 26 and then remove the remainder of the hydrocarbons in the tower through line 25 and withdraw them from the system through line 28. Removal of the higher boiling fractions, i. e. those boiling above 360–380° F., eliminates the bicyclic aromatics with the result that in the subsequent catalytic cracking operation the formation of coke and fixed gases is appreciably reduced.

The liquid collected in tank 26, whether comprising the entire bottoms from fractionating means 20 or only a selected portion thereof, is withdrawn from said tank through line 29 by means of pump 30 and forced through line 31 into and through a heating means 32, wherein the oil is heated to a temperature sufficient to maintain the required temperature in the reaction zone into which it is presently to be introduced. The heated oil flows through line 33 into a reaction zone 34 containing a catalytic material 35, the nature of which will be disclosed below.

Reaction zone 34 is maintained under conditions which promote cracking. Temperature is maintained between 750 and 950° F. and pressure between slightly above atmospheric and about 70 or 150 pounds per square inch. The rate at which the oil is passed through reaction zone 34 may be between 0.3 and 3.0 volumes of liquid oil per volume of catalyst per hour, preferably in most cases between 0.6 and 1.5 v./v./hour. The catalyst 35 in reaction zone 34 may comprise natural clays of the bentonitic and montmorillonitic type, activated clays, synthetic clays, or silica gel mixed or combined with magnesia, alumina or the like, all of which promote cracking under the conditions maintained in reaction zone 34.

Products of reaction leave reaction zone 34 through line 36, pass through a cooling means 37 and then discharge into a separating means 38. Gaseous products are removed from separating means 38 through line 39 and may be discarded, passed into the refinery fuel line or otherwise disposed of. Liquid products are removed from separating means 38 through line 40 and are forwarded by means of pump 41 to fractionating means 20 so that an aviation gasoline fraction may be segregated therefrom and the fractions boiling above the aviation gasoline range or only a portion thereof may be recycled through the catalytic cracking operation.

In the operation of the process, it will be understood that many variations may be made within the scope of the invention. For example, heat exchange between the hot outgoing products and the cold incoming materials may be employed where feasible and the catalyst, instead of being used in fixed or stationary form as shown in the drawing, may be used in finely divided or powdered form suspended in the reaction materials. When powdered catalysts are used in reaction zones 11 and 34 respectively, it will be understood that suitable means, such as cyclone separators, for separating the powdered catalysts from the reaction products will of course be required. Except for mechanical changes made necessary by the use of powdered catalysts, the operating conditions will in general be similar to those used in operation with fixed or stationary catalysts. One type of operation with powdered catalysts which is especially advantageous is what may be called "fluid catalyst" operation. In this type of operation the mixture of reacting vapors and powdered solid catalyst behaves in much the same way as a liquid and is subject to the same laws with respect to density, static head and the like as a liquid. The ratio of powdered catalyst to vapors is relatively high and the length of time the catalyst remains in the reaction zone may be substantially longer than the length of time the reacting vapors remain therein. The velocity of the catalyst through the reaction zone is therefore less than could be the case in an ordinary powdered catalyst system in which the powdered solid material is carried along at substantially the same velocity as the reacting vapors.

It will be found that both catalysts 12 and 35 in reaction zones 11 and 34 respectively gradually lose their activity in promoting the desired reactions because, it is believed, of the formation or deposition thereon during the reaction of carbonaceous contaminants such as coke. When the activity of these catalysts has been reduced to such an extent that the desired results are not obtained, their activity may be restored by a regeneration treatment which consists in burning off the carbonaceous contaminants. This is accomplished by passing hot inert gases containing regulated quantities of air or oxygen through the catalyst mass until the carbonaceous contaminants are eliminated by combustion. Because of the necessity for periodic regeneration of catalysts 12 and 35, it is usually desirable to provide two or more reaction zones similar to reaction zones 11 and 34 respectively so that while the catalyst in one reaction zone is being regenerated, the flow of oil may be diverted to another and similar reaction zone.

The following example illustrates the application of the invention:

A virgin heavy naphtha derived from an East Texas crude and having the following characteristics:

Gravity __________ °A. P. I.	50.9
Initial boiling point __________ °F.	228
Final boiling point __________ °F.	401
Octane No. A. S. T. M.	43.9
Aniline point __________ °F.	128

is subjected to catalytic reforming in the presence of hydrogen under the following conditions:

Catalyst	(1)
Temperature __________ °F.	958
Pressure __________ lbs./square inch	250
Oil feed rate __________ v./v./hour	0.76
Recycle gas rate__cubic feet/barrel of oil	2,990
Per cent hydrogen in gas	56
Length of reaction portion of cycle__hours	6

The liquid products obtained are separated into two fractions, one comprising an aviation gasoline having an end point of about 300° F. and the other comprising hydrocarbons boiling above about 300° F. and having a boiling range between 300 and 439° F. by Engler distillation.

The latter fraction, i. e. the one boiling between 300 and 439° F., is divided into two portions. One portion (A) is subjected to catalytic cracking without further fractionation and the other portion is fractionated to obtain a fraction comprising about 76% of said portion. This is done to eliminate the highest boiling fractions of said portion and the fraction (B) so obtained has a boiling range between 292 and 365° F. by Engler distillation. A and B are then subjected to catalytic cracking under the following conditions:

Catalyst	Synthetic silica alumina
Temperature __________ °F.	850–860
Pressure	Atmospheric
Feed rate __________ v./v./hr.	0.6
Length of reaction portion of cycle, hours	2

[1] Aluminum and molybdenum oxides.

The products obtained and the important characteristics thereof are as follows:

	Feed A	Products from A (300–439° F.)	Products from B [2] (292–365° F.)
Coke: Percent on feed to reactor		4.9	3.2
Gas, C_3 and lighter: per cent on feed to reactor		9.8	8.8
C_7 aromatics (210–260° F.):			
Percent on feed to reactor	0	6.2	8.9
Gravity ______ °API		39.9	39.3
Aniline point ____ °F		[1] −37	[1] −17
Olefins ______ percent		5.0	6.0
Aromatics ______ do		55.0	57.0
Naphthenes ____ do		6.0	37.0
Paraffins ______ do		34.0	0
C_8 aromatics (260–310° F.):			
Percent on feed to reactor	0.9	24.8	33.2
Gravity ______ °API	38.4	35.3	35.5
Aniline point ____ °F	3	[1] −55	[1] −27
Olefins ______ percent	6.0	3.0	2.0
Aromatics ______ do	64.0	82.0	66.0
Naphthenes ____ do	0	4.0	0
Paraffins ______ do	30.0	11.0	32.0

[1] Extrapolated.
[2] Feed B is 76% overhead from feed A.

It will be noted that catalytic cracking of both A and B effects a reduction in boiling range to the range of aviation gasoline without any appreciable change in the aromatic content. A comparison of the products from A and B shows an advantage for the latter in that less coke and gas are produced for approximately the same reduction in boiling range. As a result of the catalytic cracking of the fractions of the catalytically reformed product which boil above the range of aviation gasoline, it will be seen that a substantial amount of additional aromatic hydrocarbons boiling in the aviation gasoline range are obtained.

This invention is not limited by any theories of the mechanism of the reactions nor by any details which have been given merely for purposes of illustration but is limited only in and by the following claims in which it is intended to claim all novelty inherent in the invention.

I claim:

1. A process for the conversion of heavy naphtha into aviation gasoline having a high concentration of aromatics which comprises passing said heavy naphtha to be converted through a reforming zone, contacting said heavy naphtha fraction within said reforming zone with an aromatizing catalyst, maintaining said heavy naphtha in contact with said aromatizing catalyst while at active reforming temperature for a period sufficient to convert a substantial portion of said naphtha into aromatic constituents, thereafter fractionating the reformed products to segregate a lower boiling fraction in the aviation boiling range and a higher boiling fraction boiling between about 300 and 360–380° F., passing said higher boiling fraction through a cracking zone, contacting said higher boiling fraction within said cracking zone with an active cracking catalyst of a composition different from said aromatizing catalyst, maintaining said oil while at active cracking temperature in contact with said cracking catalyst for a period sufficient to crack a substantial portion of said higher boiling fraction into aviation gasoline constituents, and thereafter fractionating the cracked products to segregate an aviation gasoline therefrom.

2. The process defined by claim 1 wherein hydrogen is mixed with the heavy naphtha fraction passing through said reforming zone.

3. In the process defined by claim 1, the fur-

ther improvement which comprises employing an aromatizing catalyst comprising alumina and a group VI metal oxide.

4. In the process defined by claim 1, the further improvement which comprises employing a cracking catalyst comprising silica and alumina.

5. A process for the conversion of heavy naphtha into aviation gasoline having a high concentration of aromatics which comprises passing said heavy naphtha to be converted through a reforming zone, contacting said heavy naphtha fraction within said reforming zone with an aromatizing catalyst, maintaining said heavy naphtha in contact with said aromatizing catalyst while at active reforming temperature for a period sufficient to convert a substantial portion of said naphtha into aromatic constituents, thereafter fractionating the reformed products to segregate a lower boiling fraction in the aviation gasoline boiling range, an intermediate boiling fraction boiling above the aviation boiling range but below the boiling range of condensed ring bicyclic aromatic hydrocarbons, and a heavier fraction containing said condensed ring bicyclic aromatic hydrocarbons, passing said intermediate fraction through a cracking zone, contacting said intermediate fraction within said cracking zone with an active cracking catalyst, maintaining said fraction in contact with said catalyst while at active cracking temperature for a period sufficient to convert a substantial portion of said fraction into lower boiling constituents in the aviation boiling range, and thereafter fractionating the cracked products to segregate an aviation gasoline fraction therefrom.

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