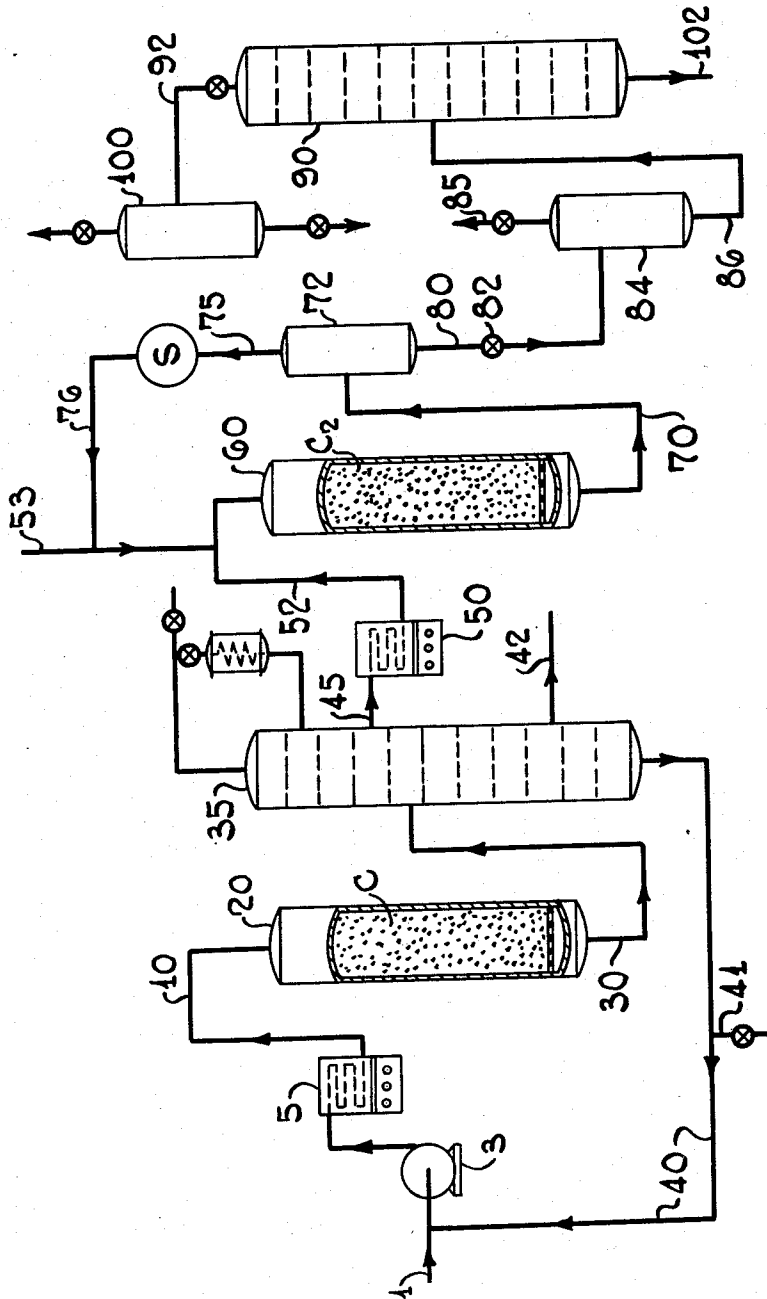


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CATALYTIC CRACKING AND REFORMING PROCESS
FOR THE PRODUCTION OF AVIATION GASOLINE
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CATALYTIC CRACKING AND REFORMING
PROCESS FOR THE PRODUCTION OF
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8 Claims. (Cl. 196—49)

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The present invention relates to the novel features hereinafter disclosed in the specification and claims.

It is of course a matter of record and common practice at the present time, to form aviation base gasoline by catalytic cracking employing any one of several commercial operations, including the stationary bed type of operation where the vapors to be cracked pass through a case or reactor containing one or more beds of catalyst; to cause the vapors to flow countercurrent or concurrent with a moving granular catalyst in a cracking zone, or to contact the hydrocarbon vapors to be cracked with a powdered catalyst in the so-called "fluid catalyst" type of operation.

My present improvements include any of the known methods of catalytic cracking, coupled with the concept of subjecting the cracked gasoline to a reforming operation in the presence of added hydrogen for the purpose of improving its octane rating by causing saturation of branch chain olefins which are invariably present in the cracked gasoline, and aromatizing cyclic olefins, naphthenes, and the like, which are also present therein.

I am aware that prior to this invention others have catalytically cracked a gas oil to form cracked gasoline, and I am also aware that prior to this invention others have reformed virgin naphthas to increase the aromaticity and otherwise improve the anti-detonation qualities of the said naphtha. However, as far as I am aware, my present combination of steps wherein I crack catalytically a suitable feed stock to form cracked gasoline and then subject the cracked gasoline to reforming in the presence of added hydrogen and a highly effective catalyst, such as MoO_3 on charcoal or zinc spinel has not previously been performed by others and/or disclosed in the prior literature. I deem the advantages of my invention to be that, since the cracked gasoline contains olefins, predominantly branch chain olefins, these olefins become saturated during the reforming to form branch chain paraffin compounds and, at the same time, naphthenes which are present in the cracked gasoline are converted to aromatics boiling in the aviation gasoline range, so that the product issuing from the reforming step is enriched in isoparaffins or branch chain paraffins and in aromatics boiling in the aviation gasoline range.

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The main object of my present invention therefore is to produce an aviation gasoline of improved octane number, lead susceptibility, and low acid heat.

A secondary object of my invention is to retreat catalytically cracked aviation gasoline under conditions which will increase the aromaticity and branch chain paraffin content of the cracked aviation gasoline and, at the same time, effect the desired result in an expeditious and economical manner.

Other and further objects of the present invention will appear from the following more detailed description and claims.

To the accomplishment of the foregoing and related ends, I first subject a suitable feed stock, such as an East Texas gas oil boiling within the range of, say, from 400° F. to 800° F. to catalytic cracking, subject the cracked products to fractional distillation, and then subject a fraction boiling in the aviation gasoline range to contact with an effective reforming catalyst, such as a VI group oxide supported on a suitable base or spacing agent at high temperatures and high pressures in the presence of added hydrogen and thereby obtain an aviation gasoline of improved quality.

In the accompanying drawing, I have shown a flow plan which illustrates diagrammatically a preferred modification of my invention.

Referring in detail to the drawing, a suitable gas oil, such as a virgin gas oil boiling in the range of 400° F. to 800° F. or thereabouts and derived from an East Texas crude, is introduced into the system through line 1, thence passed by a pump 3 into a suitable heating means 5, such as a fired coil or other suitable means, and thence withdrawn from the heating means through line 10 and passed into a cracking case 20 containing a suitable cracking catalyst C in the form of one or more stationary beds, the catalyst itself being a synthetic gel catalyst made in known manner and containing silica and alumina gels or silica and magnesia gels. Of course, the catalyst may also consist of known cracking clays, such as acid-treated bentonitic clays. The conditions for cracking are also well known and generally the cracking is carried out at relatively low pressures, say, 5 to 10 lbs. per square inch, in the cracking case 20, and at temperatures in the range of from about 850° F. to 925° C., the feed rate

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to the cracking case being such that the feed is resident in the reaction zone for 5 to 30 seconds, with 15 to 20 seconds giving good results. As I have previously pointed out, the cracking may be carried out using the fluid catalyst technique, such as disclosed in the application of Campbell et al., Serial No. 371,923, filed December 7, 1941.

The cracked products are withdrawn from the reactor, in the modification I have shown, through line 30 and are then subjected to segregation of various fractions by fractional distillation which may be accomplished in any convenient method, such as a fractionating tower 35 provided with reboiling and refluxing and the other conventional accessory apparatus usually associated with the type of equipment to effect the desired results. From the bottom of the tower 35, I may withdraw the unconverted gas oil through line 40, this material being usually known as "cycle oil," and return it for further treatment in the process through line 1. A portion of said cycle oil may be continuously withdrawn from the system as it becomes excessively refractory.

A side stream may be withdrawn from the tower 35 through line 42, this material being, say, a kerosene or a heating oil, and it may be treated in any known manner to recover a desirable product. My invention, however, is concerned with the fraction withdrawn as a side stream through line 45 containing, say C₄ and/or C₅—325° F. end boiling point fraction, which I subject to catalytic reforming in a manner presently to be described. It will be understood that in the cracking operation I have previously described, the skilled petroleum engineer will realize that a number of commonly used expedients and accessory apparatus will be used, such as additional pumps, flow meters, heat exchangers, and the like, in order to improve the operation, but for simplicity and to emphasize my own improvements I have omitted a showing of these expedients in the drawing.

Referring to the fraction recovered through line 45, the same is reheated in a suitable heating means which may be a fired coil 50, thence withdrawn through line 52, mixed with a hydrogen-containing gas in 53 and discharged into a reaction vessel comprising a reforming zone 60 containing a suitable reforming catalyst which I have indicated at C₂. This catalyst may be a II, IV, V or VI group oxide or sulfide, or a mixture thereof, supported or carried on a suitable spacing agent, such as alumina, for instance, so-called "activated alumina" or any other suitable carrier. Thus, a good catalyst for use in the reformer 60 would be one containing about 8 to 12 weight per cent molybdenum oxide distributed through or carried on 92 weight per cent of charcoal. Another good catalyst would be one in which zinc spinel (ZnAl₂O₄) was used as the base or support, instead of the "activated alumina." For instance, an excellent hydroforming catalyst is one containing 10 weight per cent MoO₃, 90 weight per cent zinc spinel. CrO₃ could also be used in place of the MoO₃, as well as the usual dehydrogenation oxides.

The feed stock entering through line 52, as previously indicated, usually contains naphthenes and branch chain olefins. It is one of the purposes of the treatment in the reformer 60 to convert branch chain olefins into branch chain paraffins by hydrogenation of said olefins and, at the same time, to aromatize the naphthenes, such as cyclohexane, methylcyclohexane, ethylcyclopentane, and the like, which will be contained in

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appreciable quantities in the said feed entering the reformer. In addition to the catalysts which I have previously disclosed as being suitable, the following conditions are maintained within the reformer:

Temperature.....	875-950° F., preferably 910-930° F.
Pressure.....	100-400 lbs. per sq. in. gauge, with about 200-250 lbs. per sq. in. gauge preferred.
Feed Rate.....	0.5-2 vols. of liquid feed per vol. of catalyst per hr., with about 1-2 v./v./hr. preferred.
Hydrogen (Standard conditions).....	2000-4000 cu. ft. of hydrogen per barrel of oil.

Under the conditions which I have indicated above, the desired conversion takes place, and the improved gasoline is withdrawn through line 70 and passed into a separation drum 72 from which a hydrogen-containing gas is withdrawn overhead through line 75, and since it contains appreciable quantities of hydrocarbons, i. e. normally gaseous hydrocarbons, it is preferable to subject it to a scrubbing operation in a suitable scrubber which I have indicated as S, where it is treated with a light naphtha to dissolve out at least a portion of the hydrocarbons and to produce a raffinate enriched in hydrogen, which hydrogen may then be returned by line 76 to line 53 and eventually to the reformer.

The bottoms from primary separator 72 are withdrawn through line 80 carrying a pressure-reducing valve 82 and then passed into a low-pressure separator 84 from which a further quantity of normally gaseous hydrocarbons, say, C₁ to C₃ hydrocarbons, may be recovered overhead through line 85, while the remainder of the material is withdrawn through line 86 and subjected to fractional distillation in a fractionating column 90 of the usual construction and design, from which the raw aviation gasoline base may be recovered overhead through line 92 and collected in a suitable receiving drum 100. The heavier bottoms may be withdrawn from fractionating column 90 through line 102, and if desired recycled to the reformer or otherwise disposed of.

In order to show the advantages of my invention, I set forth below specific examples indicating the value and utility of my present improvements:

Example 1

An East Texas cracked gasoline from a virgin gas oil which was cracked at 930° F., taking 65% conversion of gas oil to gasoline, was subjected to hydroforming. The fraction to be hydroformed boiled up to 350° F. and was subjected to hydroforming in the presence of a catalyst consisting of molybdenum oxide on charcoal in a reaction zone maintained at 900° F. average temperature and under a pressure of 215 lbs. per square inch gauge. 2500 cu. ft. of hydrogen-containing gas per barrel of oil were fed to the reactor. The feed rate of the oil was 2 volumes of oil per volume of catalyst per hour. In the table below, I set forth the improvement in aromatic content and reduction in olefin content of four fractions of the product as compared to the original feed:

	Feed	Product	Feed	Product
Boiling Range	C ₁ —200° F.		200-350° F.	
Aromatics.....	2.6	3.2	57.0	60.0
Naphthenes.....	9.4	8.1	19.4	8.9
Paraffins.....	44.6	86.9		20.1
Olefins.....	43.4	1.8	18.4	2.0
Non-Cyclics.....	88.0		23.6	
Acid Heat, °F.....	174	6	51	10

It will be noted that the feed stock in the C₅-200° F. fraction contained almost no aromatics, but did contain 43.4% olefins, while the 200-350° F. contained 57% aromatics and 18.4% olefins. The increase in aromaticity and decrease in olefin content with increased boiling is typical of catalytically cracked products in this boiling range. It can be seen from the data that there was an increase in the aromatic content and a large decrease in the olefin content.

Example 2

In this example, operating on the same feed stock as in Example 1, and using the same catalyst but operating at a temperature of 950° F. and a feed rate of 0.5 volumes of oil per volume of catalyst per hour, I obtained the results shown below. In the table below the analytical distillation was with respect to the C₅-350° F. and the 200-350° F. fraction:

	Feed	Product	Feed	Product
Boiling Range	C ₅ -350° F.		200-350° F.	
Aromatics.....	25.8	33.0	57.0	89.6
Naphthenes.....	14.4	8.7	19.4	1.1
Paraffins.....		54.9		8.8
Olefins.....	33.3	3.4	18.4	0.5
Non-Cyclics.....	59.8		23.6	
Acid Heat °F.....	125	9	51	3

At the more severe conditions it will be noted that the C₅-350° F. fraction contained 33% aromatics as compared with 28.5% feed, and that the olefins were reduced from 33.3% to 3.4%, the acid head of the material being reduced from 124 to 9. The table also shows that the 200-350° F. fraction underwent a large change in aromaticity compared to the original feed, this 200-350° F. fraction having 89.6% aromatics following the hydroforming.

In describing the reforming phase of my invention, and in particular depicting that step in the drawing, I have, as in the case of the cracking step, omitted a showing of many conventional devices and accessory apparatus which are commonly used and well known to petroleum engineers, in order to simplify the explanation and direct attention to my own improvements. I have also omitted a description of what the petroleum engineer would recognize as necessary in the regeneration of the cracking catalyst and the reforming catalyst. The regeneration of these catalysts usually accomplished by treatment at elevated temperatures with a free oxygen-containing gas has been described in the prior literature and prior patents and other sources, and it is unnecessary to set forth herein a description of the method of regenerating the catalyst. It will be sufficient to say that any known safe and rapid method for regenerating the cracking and/or reforming catalyst may be employed when necessary.

As previously indicated, I prefer to use a hydroforming catalyst containing ZnAl₂O₄ (zinc spinel) or charcoal as the support for MoO₃, CrO₃, etc., the oxides being active oxides. However, the presence of the zinc spinel has been shown to increase the aromaticity of the product for it causes an increase in the amount of straight chain paraffins and/or olefins converted to aromatics during the hydroforming operation. Also, of course, branched chain olefins are dehydrogenated to isoparaffins, and naphthenes are dehydrogenated during the said hydroforming operation. All of these desired reactions are aided by the

presence of zinc spinel as the catalyst base. The process is so operated that the production of hydrogen during hydroforming at least equals consumption thereof and preferably exceeds it.

Numerous modifications of the present invention will suggest themselves to those who are familiar with this art.

What I claim is:

1. The method of producing high quality aviation gasoline which comprises cracking a gas oil in the presence of a synthetic alumina-silica gel catalyst, recovering a fraction boiling in the gasoline range from said cracking step, and subjecting said fraction to reforming at elevated temperatures and in the presence of a dehydrogenation catalyst which comprises about 10% of a 6th group metal oxide and about 90% of a zinc spinel base which carries the 6th group metal oxide and added hydrogen whereby the cracked gasoline is converted to a product of low acid heat and increased aromaticity and isoparaffinity without net consumption of hydrogen.

2. The method of claim 1 in which the reforming catalyst is chromium oxide on zinc spinel.

3. The method of claim 1 in which the temperature in the reforming zone is from 875° F. to 950° F.

4. The method of claim 1 in which 2000 to 4000 cubic feet of hydrogen are fed to the reforming reaction per barrel of oil.

5. The process of claim 1 in which there is no net consumption of hydrogen during the reforming operation.

6. The method of producing an aviation gasoline base of high aromaticity, branch-chain paraffinic content, and low acid heat which comprises subjecting a gas oil to catalytic cracking, recovering a cracked fraction boiling in the gasoline range and subjecting said cracked fraction to the catalytic reforming in the presence of a dehydrogenation catalyst comprising about 10% molybdenum oxide supported on about 90% zinc spinel, and added hydrogen whereby branch-chain olefins in the cracked gasoline are converted to branch-chain paraffins, naphthenes are converted to aromatics, and normal paraffins are aromatized without net consumption of hydrogen.

7. The method of producing an aviation gasoline base of high aromaticity, branch-chain paraffinic content, and low acid heat which comprises subjecting a gas oil to catalytic cracking, recovering a cracked fraction boiling in the range from about 200° F. to 350° F. and subjecting said cracked fraction to the catalytic reforming in the presence of a dehydrogenation catalyst comprising about 10% molybdenum oxide supported on about 90% zinc spinel, and added hydrogen whereby branch-chain olefins in the cracked gasoline are converted to branch-chain paraffins, naphthenes are converted to aromatics, and normal paraffins are aromatized without net consumption of hydrogen.

8. The method of producing high quality aviation gasoline which comprises cracking a gas oil in the presence of a synthetic alumina-silica gel catalyst, recovering a fraction boiling in the gasoline range from said cracking step, and subjecting said fraction to reforming at elevated temperatures and in the presence of a dehydrogenation catalyst which contains 10 weight per cent MoO₃ and 90 weight per cent zinc spinel and added hydrogen whereby the cracked gasoline is converted to a product of low acid heat

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and increased aromaticity and iso-paraffinicity
without net consumption of hydrogen.

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