Oct. 17, 1944. B. E. ROETHELI 2,360,622

METHOD OF PRODUCING AVIATION GASOLINE

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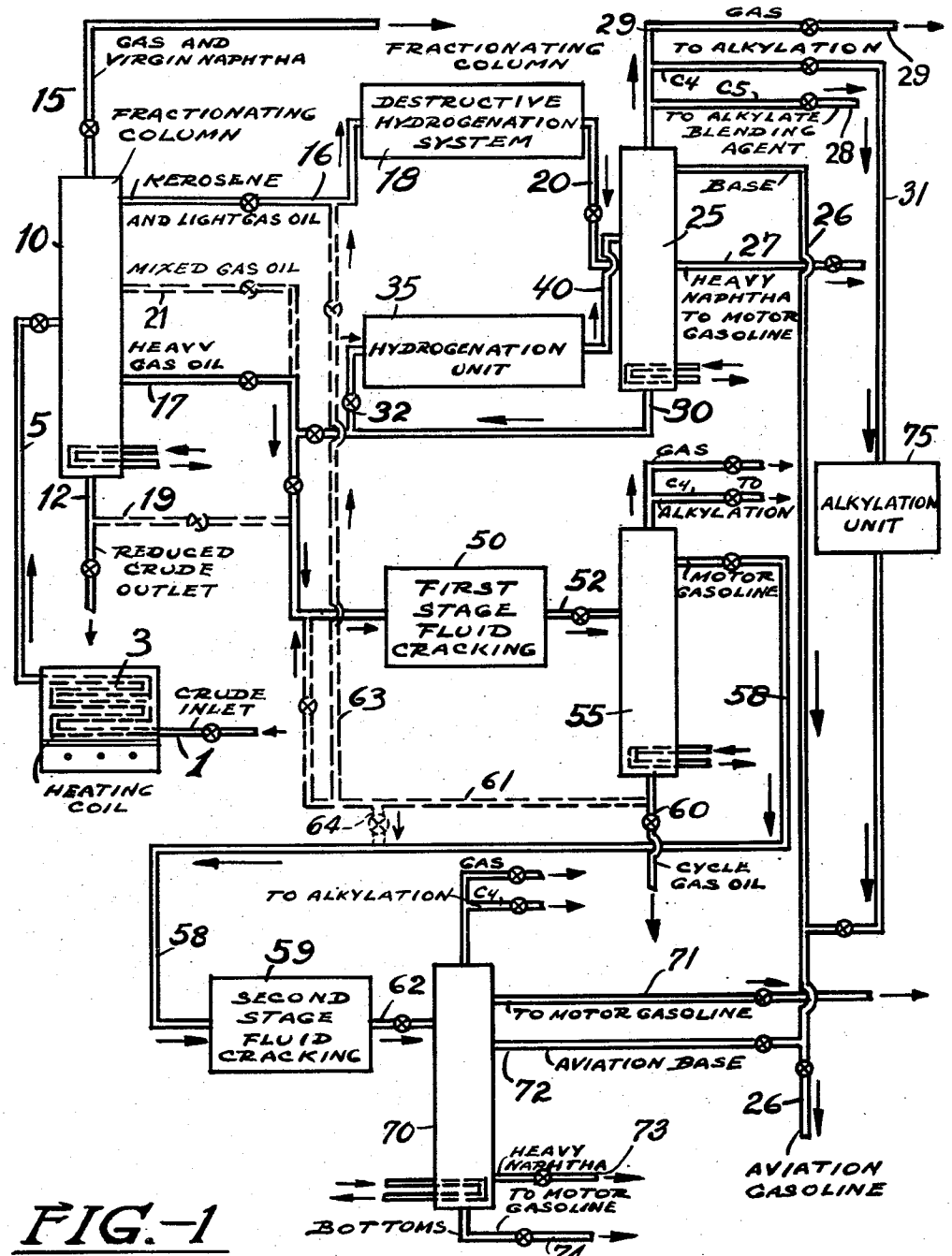


FIG.-1

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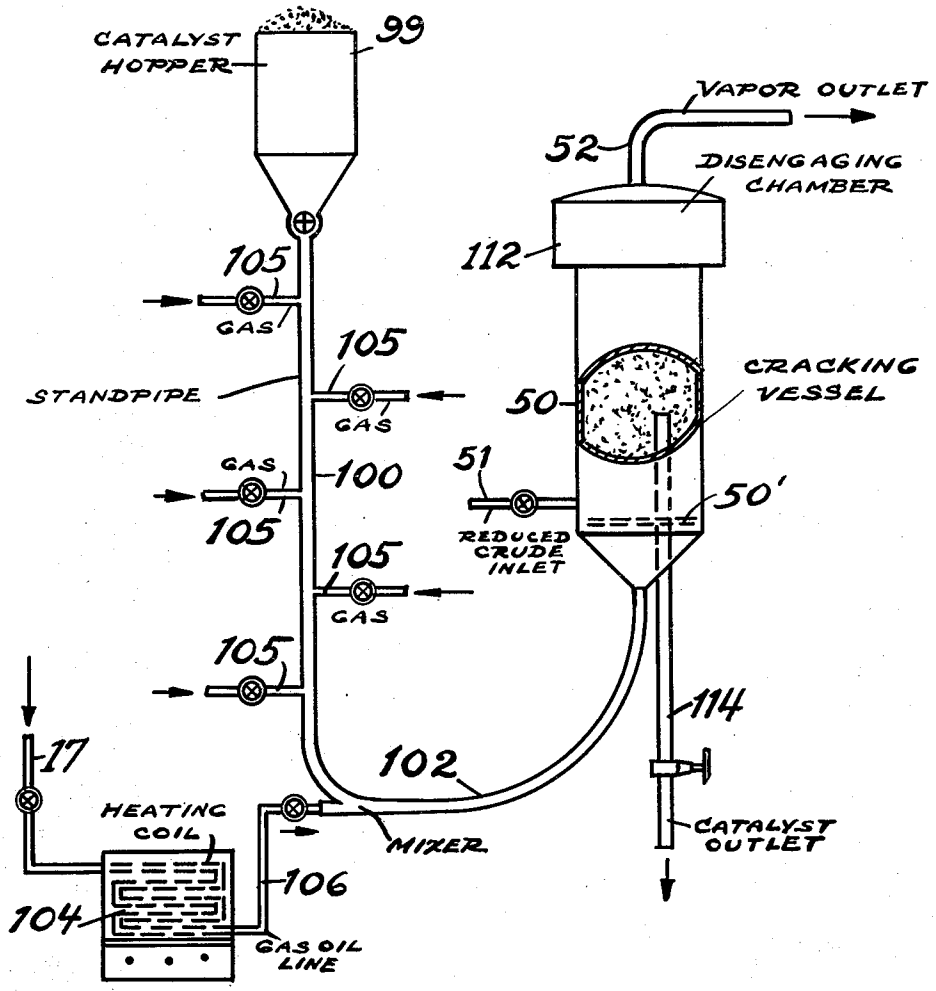


FIG. —II

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METHOD OF PRODUCING AVIATION GASOLINE

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Application April 30, 1943, Serial No. 485,129

6 Claims. (Cl. 196—53)

The present invention relates to improvements in the production of aviation gasoline and has for its main object the production of a maximum quantity of high octane number gasoline from a crude petroleum oil.

The main object of this invention is to treat, in an integrated process, a crude petroleum oil to produce, by destructive hydrogenation of the kerosene or light gas oil fraction of the crude oil, and by catalytic cracking of the heavier gas oil, followed by separate fractionation of the products of both processes, blends of certain components of the hydrogenated and cracked products yielding an aviation base fuel of superior quality.

In explanation of the preceding object, it is pointed out that the fraction of the hydrogenated product boiling up to about 200° F. and the fraction of the catalytically cracked product boiling from about 200° to 350° F. form a blend of superior anti-detonation qualities. On the other hand, the fraction of the hydrogenated product boiling above about 200° F. and the fraction of the catalytically cracked products boiling below about 200° F. do not possess good anti-detonation characteristics.

Another object of my invention is to utilize, for producing alkylate, the olefins and isoparaffins produced in the system for blending with the aviation base stocks produced by hydrogenation and catalytic cracking, and also to employ the formed isopentane as a blending agent.

Other and further objects of my invention will appear from the following description and claims.

For a better understanding of my invention reference is made to the accompanying drawings in which I have shown in Fig. I diagrammatically, a preferred modification of my invention; and in Fig. II, I have shown a cracking vessel and means for feeding catalyst and oil thereto.

Referring in detail to the drawings, a crude petroleum oil, preferably one which is highly naphthenic, is introduced into the system through line 1 and is then heated in a fired coil 3 to a temperature of from 800–900° F., whereupon it is discharged through line 5 into a fractionating column 10. From fractionating column 10 I recover as bottoms through line 12 a heavy residual reduced crude, this reduced crude amounting to about 10–20% by volume of the orginal feed. The reduced crude recovered through line 12 may be withdrawn from the present system and subjected to coking or viscosity reducing to produce further quantities of gas oil, or it may be subjected to cracking as will subsequently more fully appear hereinafter. Overhead through line 15 I recover normally gaseous components and virgin naphtha. A kerosene or light gas oil fraction boiling say from 375–600° F. is withdrawn from the fractionating column 10 through line 16 and thence after suitable heating is subjected to destructive hydrogenation in a system which I have designated as 18. The hydrogenation is preferably carried out by heating the oil to a temperature of around 700° F. and conducting it to a hydrogenation zone containing a catalyst such as tungsten sulfide, iron sulfide, molybdenum sulfide or the like, supported on activated alumina or activated clay. The oil is fed to the reaction zone at a rate of 0.5 to 2.0 volumes of oil per volume of catalyst per hour. Hydrogen in the amount of 6000–20,000 cu. ft. per barrel of oil is also fed to the hydrogenation reactor and a pressure of from 150–1000 atmospheres is imposed upon the hydrogenation system, whereupon the kerosene fraction undergoes destructive hydrogenation to form fractions of gasoline boiling range and other products.

The products of the hydrogenation step are passed through line 20 into a fractionating column 25 where they are subjected to fractionation as follows: First, a heavy bottoms fraction is withdrawn through line 30 and it may be recycled through line 32 to a second hydrogenation unit 35, operated similarly in all respects to hydrogenator 18 and thereafter the hydrogenation products from this second hydrogenation zone are returned through line 40 to fractionator 25, or the heavy bottoms fraction may be discharged into line 17 leading to a cracker, as will appear presently. Second, a heavy naphtha boiling from about 200° to 400° F. or higher is withdrawn from fractionator 25 through line 27. The fraction does not possess sufficiently high anti-detonation quality to make it a desirable aviation fuel, but it is satisfactory for use as an automotive fuel and may be blended with other constituents of gasoline to make a finished product of suitable boiling range and volatility. Third, the most important fraction, from the standpoint of this process is recovered from fractionator 25 through line 26. This fraction boils up to 200° F. and contains the saturated hydrocarbons above the C_5 fraction. It possesses a high octane number and hence forms a valuable component of aviation gasoline. Finally, from the fractionator 25, I recover separately through line 28 C_5 hydrocarbons including isopentane which may be added to aviation gasoline to increase volatility and also through line 31 a C_4 fraction containing iso-

butane, which isobutane may be alkylated with the olefins formed in other parts of the present system. The disposition and use of the C_5 and C_4 hydrocarbons will be explained subsequently herein. Methane, ethane, propane, etc., are rejected from the system through pipe 29. The separation of the C_1 to C_5 hydrocarbons is merely indicated in the drawings diagrammatically for purposes of simplicity of explanation, but the expert will understand that actually additional distillation towers (not shown) will be required to effect the indicated separation by conventional means.

Referring again to fractionator 10, a heavy gas oil, that is a gas oil boiling from 600–800° F., is withdrawn from the fractionator through line 17 and thence subjected to a catalytic cracking operation in a unit 50. The details of operation of the unit 50 will be described in more detail hereinafter. Suffice it to say for the moment, that oil is cracked and the cracked products are withdrawn from the unit 50 and discharged through line 52 into a fractionator 55 where they are subjected to fractionation. From fractionator 55 a gasoline fraction is withdrawn through line 58 and subjected to a second stage of catalytic cracking in a unit 59. The cracked products from the second stage are withdrawn through line 62 and discharged into a fractionator 70. From fractionator 70 there is recovered through line 71 a motor gasoline fraction, through line 73 a heavy naphtha fraction, through line 74 a motor gasoline bottoms product, and through line 72 a naphtha boiling in the aviation range which is combined with the lighter (lower boiling) aviation base stock recovered through line 26 from fractionator 25, which latter fractionator contained the products resulting from the hydrogenation of the kerosene or light gas oil. Now the naphtha recovered through line 72 boils from about 200° to 350° F. and is superior in octane number to the fraction boiling up to 200° F. Hence by combining the fraction in 26 from the hydrogenation unit with the fraction in 72 from the cracking steps, I secure a blended base aviation gasoline of very high octane number, and as stated this feature of producing and combining the specified components goes to the hearth of this invention.

From fractionator 55 as indicated in Fig. I, there is also obtained a cycle stock through line 60 which may be recycled through line 61 or line 64, respectively, to the first or second stage of cracking or to the hydrogenation stage. A portion of this fraction may be rejected from the system. Also from fractionator 55, C_4 olefinic hydrocarbons, may be recovered and alkylated with an isoparaffin in known manner. Lighter hydrocarbons may be rejected from the system, as indicated. The separation of C_5 and lighter hydrocarbons is effected in known manner.

I have described thus far, a method of producing an aviation base stock from a crude petroleum oil and it involved separating from the crude oil, a light gas oil (or kerosene) and subjecting that light gas oil to destructive hydrogenation to form a component of the aviation base gasoline boiling up to 200° F.; also separating from the crude oil, a heavier gas oil which is cracked to form cracked gasoline, which cracked gasoline is recracked catalytically, and from this recracked gasoline, the heavier ends, i. e., the 200° to 350° F. fraction is recovered from the second stage of cracking and blended with the naphtha boiling up to 200° F. produced from the hydrogenated kerosene or light gas oil.

Referring now to Fig. II, I shall describe in detail a fluid catalyst cracking operation. The unit 50 of Fig. I comprises in a preferred modification, shown in Fig. II, the following essential apparatus; first, a feed means standpipe 100 is in communication with an elevated hopper 99 containing the cracking catalyst in the form of a powder having an average particle size of around 300 mesh, although it may vary from 200–400 mesh. This catalyst may be removed from standpipe 100 and discharged into a line 102 where it is mixed with the heavier gas oil from line 17 and fractionator 10, after the said gas oil has been heated in a furnace or fired coil 104 to a temperature of around 850° to 1000° F. The vaporized gas oil is withdrawn from the fired coil 104 through line 106 and discharged into the pipe 102 containing catalyst (as described above) and thereafter the mixture is discharged into a cracking vessel 50 wherein the superficial velocity of the vapors is regulated or controlled within the limits of 0.5 to 6 ft. per second, preferably 1 to 2 ft. per second, so as to form within reactor 50 a dense, turbulent, fluidized mass of catalyst intermixed with the vapors. It should be pointed out that in order to aid in the fluidization of the catalyst descending through standpipe 100, a plurality of gas taps 105 are provided at spaced points in the standpipe through which some gaseous material (e. g., normally gaseous hydrocarbons) may be forced into the standpipe so as to cause the fluidization of the catalyst therein, this gas ascending at a relatively low velocity, say 2–3 ft. per second, and effecting the fluidization of the catalyst and rendering it capable of flowing freely, like water, through the system in the manner indicated.

Within the reactor 50 the temperature is from 850–1000° F., the concentration of catalyst being such that the fluidized mass weighs from 15–25 lbs. per cu. ft., and a pressure of 0 to 15 lbs. per square inch above atmospheric is maintained within the reactor. The residence time is such that the vapors reside in the reaction zone for 10–40 seconds.

The vapors pass upwardly into a suitable separating device 112 which is herein shown to be a section of greater diameter than the lower portion of the reactor. The catalyst entering therein reverses direction and gravitates towards the catalyst in the main body of the reactor and the vapors are therefore depleted considerably of catalyst, the separation being induced or caused by the fact that the linear velocity of the gases in the disengaging chamber 112 is reduced by the increased diameter to the order of ½ ft. per second. The catalyst is continuously withdrawn from reactor 50 through line 114, and this catalyst may be regenerated by burning off its contaminants with air, in apparatus not shown, and thence returned to feed hopper 99. The details of regeneration of the catalyst are well known to the art and need not be discussed herein, but preferably the catalyst is regenerated in the form of a fluidized mass of catalyst in an oxygen containing gas, having approximately the same density as the mixture of catalyst and vapor in the reaction zone and formed in a similar manner, viz. by controlling the velocity of the gas in the regenerator within the limits heretofore prescribed for the vapors in the reactor. The vapors are withdrawn

through line 52, as indicated in Fig. I, and they may be treated as hereinbefore described. It should be pointed out of course that it may be desirable to insert in line 52 dust separators, cyclone separators, electrical precipitators, and the like to separate the last traces of catalyst.

The second stage cracking unit 59 may be of the same construction and operated in the same manner as 50 illustrated in Fig. II, and it is deemed unnecessary to repeat the description. Suffice it to say that the gasoline is heated and passed through unit 59 at a temperature of from 850–1000° F. in the presence of an active cracking catalyst. The cracking catalyst used in my process may be an acid treated clay of the bentonitic or montmorillonite type, but preferably it is a mixed or plural gel containing alumina or magnesia and silicia. For example, an excellent catalyst containing 10 to 20% by weight alumina, the remainder silica gel may be employed.

During the operations which I have described various quantities of gas are produced. For example, there is recovered from fractionating column 25 an overhead fraction containing C_4, C_5 and lighter hydrocarbons, that is, methane, ethane, propane, etc. The C_4 fraction containing high percentages of isobutane is preferably passed through line 31 and subjected to alkylation with propylene, butylene or pentylene from towers 55 and 70 in the presence of sulfuric acid at temperatures around 30° F., in known manner, in a unit which I have designated 75 to produce an alkylate product, which alkylate product may be blended with the base gasoline components in lines 26 and 72 in the ratio of say 60–90 volume per cent of the base gasoline and the remainder the alkylation product. By thus combining the products in the manner indicated, I am enabled to produce a finished aviation gasoline approaching an octane number of 100 without lead, and by adding 4 cc. of lead tetraethyl per gallon I am able to produce an aviation gasoline having an octane number considerably in excess of 100 and exhibiting good rich mixture characteristics. Also, it is pointed out that the C_5 hydrocarbons contain some isopentane which may be blended into the alkylate product for the purpose of increasing volatility and forming with the other components an aviation gasoline of proper volatility and boiling range.

Another modification of my invention includes discharging the reduced crude in line 12 through a line 19 into the first stage of cracking in a unit such as 50, provided with conduit means adapted to permit injection of liquid oil. This oil may be injected in liquid form through pipe 51 directly into the cracking unit 50 where it contacts the catalyst which may have a temperature of around 1000° F. where it is discharged into the cracking unit directly from regeneration. In other words, if the fouled catalyst withdrawn through line 114 (Fig. 2) from cracking vessel 50 is regenerated, its temperature as it leaves the regenerator may be about 1000 F. or even higher, say 1100° F. If this hot catalyst is directly returned uncooled to the cracking zone and mixed with reduced crude recovered from column 10 at a temperature of say 400–600° F. in the ratio of 20–40 lbs. of catalyst per pound of oil, then the hot catalyst heats the oil to cracking temperatures and thus obviates the necessity of using a furnace to heat the reduced crude. In like manner the heavy gas oil in line 17 may bypass furnace 104 (Fig. 2) and be directly injected into the cracking reactor 50, if the catalyst to oil ratio is of the order indicated.

It can be seen therefore from the foregoing description of my invention that it involves primarily the destructive hydrogenation of light gas oil from a crude oil to form a light aviation base component, and the catalytic cracking of a heavy gas oil from said crude oil, the recracking catalytically of the gasoline produced in the first stage of cracking, and the fractionation of the recracked product to form a heavier aviation base component which is blended with the said light aviation base component from the hydrogenated kerosene fraction. The C_4 isoparaffin hydrocarbon and the C_3, C_4 and C_5 olefins produced in the process, are alkylated to form an alkylated product which is blended with the isopentanes formed in the process and further blended with the above aviation base components to form a high quality aviation gasoline. In the drawings I have shown by means of dotted lines alternative procedures. Thus referring to fractionator 10 I may recover a mixed gas oil fraction through line 21 as a single stream and catalytically crack it rather than to separate the gas oil into a lighter fraction for destructive hydrogenation, cracking only the heavier fraction.

Further, the C_4 cut or fraction from fractionators 25 and 70 is rich in isobutane, while the C_4 fraction from the first stage of cracking recovered from fractionator 55 is rich in butylenes. Hence, the alkylation step of my process may be, in large measure if not entirely, accomplished by reacting olefins and isobutylene formed within the present system. The heavy naphtha produced from the destructive hydrogenation and recovered through line 27 from fractionator 25 may be used as an automotive motor fuel and the virgin gasoline recovered through line 15 may be used for the same purpose.

I claim:

1. The method of producing an aviation gasoline of high octane rating which comprises charging a crude oil to a distillation zone, recovering a light gas oil from said distillation zone and a heavier gas oil from said distillation zone, subjecting the light gas oil to destructive hydrogenation, fractionating the hydrogenation products to recover a base gasoline component boiling up to 200° F., subjecting the heavier gas oil to catalytic cracking, fractionating the products to recover a cracked gasoline, recracking the cracked gasoline catalytically, fractionating the products, recovering a component boiling from about 200° to 325° F., and blending the gasoline component from the destructive hydrogenation process with the recracked cracked gasoline to form an aviation gasoline.

2. The process of claim 1 in which isoparaffins formed during the hydrogenation are recovered during the fractionation of the hydrogenation products, in which olefins formed during the catalytic cracking are recovered by fractionation of the products of the cracking operation, in which the said isoparaffins are alkylated with the said olefins to form an alkyate of gasoline boiling range and in which the said alkylate is blended with the said selected components of the hydrogenation and catalytic cracking to form aviation gasoline of superior quality.

3. A process of producing aviation base gasoline which comprises destructively hydrogenating the light gas oil of a naphthenic crude petroleum oil, recovering a light fraction boiling up to about 200° F. therefrom, catalytically cracking a

relatively higher boiling gas oil than the first mentioned gas oil, recovering gasoline from the products of the said cracking, recracking said cracked gasoline, fractionating the products to recover a heavy fraction boiling in the range of from about 200° to 350° F. and blending the light fraction from the destructive hydrogenation with the heavy fraction from the cracking to form an aviation base gasoline of improved anti-detonation quality.

4. The method of claim 3 in which the destructive hydrogenation step is effected in the presence of a hydrogenation catalyst.

5. The method of claim 3 in which the cracking steps are performed in the presence of a synthetic gel catalyst.

6. The method of claim 3 including the alkylation of isoparaffins produce in the process with olefins similarly produced and the addition of the alkylate to the base gasoline.

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