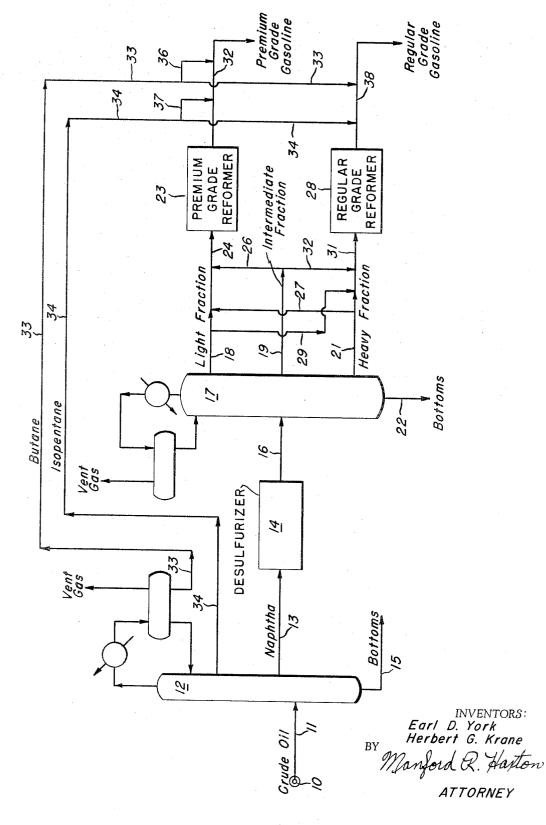
## Feb. 21, 1967

BALANCED-OCTANE GASOLINE MANUFACTURE

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#### 3,305,476

BALANCED-OCTANE GASOLINE MANUFACTURE Earl D. York and Herbert G. Krane, Gary, Ind., assignors to Standard Oil Company, Chicago, Ill., a corporation of Indiana Filed Dec. 14, 1964, Ser. No. 418,041

### 6 Claims. (Cl. 208-79)

This invention relates to an improved process for manufacturing motor gasoline having improved octane rating 10 throughout the boiling range thereof. More specifically, the invention relates to manufacture of such gasolines by catalytic reforming of selectively blended feedstocks.

There has recently been an increase in production of automobiles having manual transmissions. In cars 15 equipped with manual transmissions, particularly if the induction system alloys an appreciable degree of fuel segregation (separation of light and heavy components) at low engine speeds, the use of conventional motor gasolines results in knocking in some cylinders of the engine 20 because of the increased concentration of low-octane lowboiling components. Fuel segregation frequently occurs in induction systems under low-speed wide-open-throttle accelerations such as can occur with cars having manual transmissions. Wide-open-throttle accelerations in high 25 gear are not possible in cars having automatic transmissions. This separation of light and heavy fuel components is due to the very low velocity and low turbulence of the fuel air mixture at low engine speeds. The sudden introduction of additional fuel to the low turbulence air 30 stream results, for a short period of time, in the liquid fraction not being distributed uniformly to all cylinders.

With fuels containing high concentrations of catalytic reformate the lighter fractions consist largely of lowoctane components. Thus, when these low-octane com- 35 ponents reach the cylinder knock is likely to occur. This knock, or detonation, will discontinue only when the liquid film of heavier components on the manifold wall reaches the cylinders in an amount and at a rate sufficient to provide adequate portions of all components. Thus, 40 the knock resulting from the inevitable fuel segregation would be eliminated if a fuel were provided having substantially balanced octane across its boiling range.

Our invention provides a method of producing full boiling range motor gasoline having substantially bal- 45 anced octane across the boiling range thereof by subjecting to catalytic reforming a selectively blended reformer charge to produce a catalytic reformate having octane and boiling range characteristics such that said gasoline consists essentially only of said reformate and sufficient 50 added light hydrocarbons to impart to said gasoline the desired vapor pressure. More particularly, by our invention we provide a method of producing from low octane naphtha a motor gasoline having balanced octane across the boiling range thereof, which gasoline consists essen- 55 tially of catalytic reformate and sufficient light hydrocarbons to produce the desired gasoline vapor pressure, which method comprises distilling said naphtha to produce a low boiling fraction, and an intermediate boiling fraction and a high boiling fraction, blending portions of 60 each of said fractions to produce a reformate charge stream and subjecting said charge stream to catalytic reforming to produce a reformate having balanced octane across the boiling range thereof, and blending said reformate, without further treatment, with light hydrocar- 65 Speed Knock," SAE Summer Meeting, June 1960. The bons to produce said gasoline.

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A preferred embodiment of our invention is a process for converting low octane naphtha to produce two motor gasolines having different research octane numbers and each of said gasolines having substantially balanced octane across the boiling range thereof, by distilling the naphtha into light, intermediate and heavy fractions, preparing a first catalytic reformer charge stream by blending selected portions of each of said fractions and subjecting said first charge stream to catalytic reforming to produce a first motor gasoline having a balanced octane across the gasoline boiling range, and preparing a second catalytic reformer charge stream different from said first charge stream by blending selected portions of each of said fractions and subjecting said second charge stream to catalytic reforming to produce a second motor gasoline having a research octane number below the research octane of said first gasoline and also having balanced octane across the gasoline boiling range. Preferably, the distillation of the low octane naphtha is controlled so that the light fraction boils within the range of about 90 to 200° F., the intermediate fraction boils within the range of 100 to 300° F., and the heavy fraction boils within the range of 200 to 400° F. For producing two balancedoctane gasolines, the first charge stream preferably consists essentially of about 1 to 10 volume percent of the light fraction, 60 to 80 volume percent of the intermediate fraction, and 15 to 35 volume percent of the heavy fraction. The second charge stream for producing gasoline having a lower octane number from the gasoline produced from the first charge stream preferably consists essentially of 10 to 30 volume percent of the light fraction, 20 to 40 volume percent of the intermediate fraction and 40 to 60 volume percent of the heavy fraction. The reforming severity employed in the first reformer, producing the higher octane gasoline, is normally that required to produce at least about 90  $C_5$ + research octane number, preferably at least about 95  $C_5$ + research octane number. Smaller quantities of the light and heavy fractions are used to blend feed for the higher severity first (premium grade) reformer than are used in blending feed for the lower severity second reformer because the higher severity employed in the first reformer results in greater production of light and heavy reformate components. This selective blending of feeds improves volatility as well as providing balanced octane across the boiling range of the reformates.

Several methods have been proposed for determining the octane distribution throughout the boiling range of motor gasoline. One such test method which has proven to be satisfactory is the determination of "Delta R" octane number which provides a measure of the distribution of octane number through gasoline boiling range. It is used in describing the effect of fuel mal-distribution in automobiles on road octane ratings. It is defined as the research octane number (ASTM D-908) of the whole fuel minus the research octane number of a certain percent overhead fraction of the fuel when it is distilled rapidly by a specified procedure. A commonly used value is "Delta R<sub>75</sub>" which is the research octane number of the whole fuel minus the research octane number of the first 75 percent distilled. This method is used by several petroleum companies in their research and development work. Such a test method has been described by: Korn, J. M., and Moss, G., "Tetramethyl Lead Reduces Low research octane ratings are obtained by the usual methods. Delta  $R_{75}$  ratings in the range of about 3.0 to 10.0 are considered to be satisfactory. The addition of tetramethyl lead anti-knock agent in preference to tetraethyl lead will result in lower Delta  $R_{75}$  values.

Our invention can be understood from the description 5 of a specific embodiment in conjunction with the figure. Referring to the figure, crude oil feed from source 10 is fed via line 11 to conventional crude distillation column 12 wherein the crude oil is separated into an overhead fraction comprising butane, an isopentane side stream, 10 a naphtha side stream and a bottoms fraction which is withdrawn via line 15. The naphtha side stream is withdrawn from the crude distillation column and passed via line 13 to a conventional hydrodesulfurization unit 14. Desulfurized naphtha is passed from the desul- 15 furizer 14 via line 16 into pre-fractionator column 17. A butane and lighter gas stream is removed overhead and vented or used as fuel. Three fractions of the desulfurized naphtha are recovered from distillation column 17 as products; a light fraction boiling within the range of 20 about 90 to 200° F. is withdrawn via line 18, an intermediate fraction boiling within the range of about 100 to 300° F. is withdrawn via line 19, and a heavy fraction boiling within the range of about 200 to 400° F. is withdrawn via line 21. If desired a still higher boiling 25 bottoms material may be withdrawn via line 22 for use elsewhere. Two catalytic reformer feed streams are then produced by blending selected portions of each of the three fractions from lines 18, 19 and 21. A first catalytic reforming charge stream for processing in a premium grade 30 reformer 23 is prepared by introducing into the premium grade reformer charge line 24 selected portions of each of the three fractions so that the charge blend consists essentially of about 1 to 10 volume percent of the light fraction from line 18, about 60 to 80 volume percent of 35 the intermediate fraction from line 19 via line 26, and about 40 to 60 volume percent of the heavy fraction from line 21 via line 27. A second catalytic reformer charge blend for processing in regular grade reformer 28 is prepared by blending selected portions of each of the 4 three fractions so that the charge blend contains about 10 to 30 volume percent of the light fraction from line 18 via line 29 into regular grade reformer 28 charge line 31, about 20 to 40 volume percent of the intermediate fraction from line 19 via line 32 into line 31 and about 4 40 to 60 percent of the heavy fraction from line 21 into charge line 31.

The premium grade reformer 23 is operated at a reforming severity above about 90  $C_5$ + research octane, preferably at least about 95  $C_5$ + research octane number to produce a first reformate which is withdrawn from the reformer via line 32. A portion of each of the butane and isopentane streams distilled from the crude oil in disitllation column 12 are passed via lines 33 and 34, respectively, via lines 36 and 37 into line 32 wherein the butane and isopentane are blended with the reformate from reformer 23 to produce premium grade gasoline having the desired vapor pressure and substantially balanced octane throughout the boiling range.

The regular grade reformer 28 is operated at a reforming severity lower than the severity employed in the premium grade reformer 23. Catalytic reformate is withdrawn from regular grade reformer 28 via line 38 and blended with sufficient butane and isopentane from lines 33 and 34 to adjust the vapor pressure as desired to produce a regular grade gasoline having a research octane rating lower than the premium grade gasoline and having substantially balanced octane throughout the gasoline boiling range.

#### EXAMPLE

A hydrodesulfurized naphtha having an ASTM boiling range of 90 to 330° F., was distilled into three fractions having the properties listed in Table I.

TABLE I				
	Fractions			
	Light	Intermediate	Неаvу	
ASTM Distillation, ° F.: IBP 10% 30% 50% 70% 90% FBP Gravity, ° API	105 113 119 125 133 152 175 87.4	$175 \\ 192 \\ 207 \\ 222 \\ 236 \\ 254 \\ 270 \\ 66.3$	270 285 292 304 313 320 330 54, 9	

Selected portions of each of these three fractions were blended to produce two reformer charge streams as shown in Table II.

TABLE II

)	Composition, Vol. Percent	Premium Grade Reformer	Regular Grade Reformer
5	Light fraction Intermediate fraction Heavy fraction Gravity, ° API	$\begin{array}{c} 4.7 \\ 70.3 \\ 25.0 \\ 64.2 \end{array}$	$19.\ 6\\24.\ 7\\55.\ 6\\63.\ 3$

The premium reformer charge and the regular reformer charge streams were subjected to catalytic reforming over platinum-alumina catalyst at reforming severities of 97.0 and 83.0, research octane number respectively. Each of the catalytic reformates produced was then blended with butane and isopentane to produce premium and regular grade gasolines having the desired vapor pressure and volatility and also having balanced octane throughout the boiling range as indicated by the Delta R<sub>75</sub> ratings. The properties of each reformate and the composition and properties of each gasoline are shown in Table III.

TABLE III

)	Reformate Properties	Premium Grade Reformate	Regular Grade Reformate
5	ASTM Distillation, ° F.: IBP	184 243 277	116 137 175 221 274 324
)	90% FBP Gravity, ° API Research Octane, clear	372 49.5	824 377 57.0 83.0
5	Gasoline Composition and Properties	Premium Grade Gasoline	Regular Grade Gasoline
)	Composition, Vol. Percent: Butane	13.5 86.5 7.5	4.3 2.7 93.0 8.6 6.0

While our invention has been described with reference to specific embodiments and examples thereof, various alternatives will be apparent to those having skill in the 65 art. For example, if desired, the reformer charge streams could be held in intermediate storage and reformed separately on a blocked-out basis in a single reformer operated at higher severity to produce premium grade gasoline and at lower severity to produce regular grade 70 gasoline. Such alternatives and variations of our process are deemed to be within the scope of our invention,

Having thus described our invention what is claimed is: 1. A method of producing from low octane naphtha

motor gasoline having balanced octane across the boiling 75 range thereof, which gasoline consists essentially of cat-

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alytic reformate and sufficient light hydrocarbons to produce the desired gasoline vapor pressure, which method comprises distilling said naptha to produce a low boiling fraction boiling within the range of about 90–200° F., an intermediate boiling fraction boiling within the range 5 of about 100–300° F., and a high boiling fraction boiling within the range of about 200–400° F., blending selected portions of each of said fractions to produce a reformer charge stream and subjecting said charge stream to catalytic reforming to produce a reformate having balanced octane across the boiling range thereof, and blending said reformate without further treatment thereof, with light hydrocarbons to produce said gasoline.

2. A method for producing from low octane naphtha motor gasoline having substantially balanced octane across 15 the boiling range thereof wherein a selected charge blend is reformed to produce a reformate suitable for use as said motor gasoline without further treatment except for vapor pressure adjustment, which method comprises distilling said naphtha to produce a low boiling fraction 20 produce a regular grade gasoline and a premium grade boiling within the range of about 90-200° F., an intermediate boiling fraction boiling within the range of about 100-300° F., and a high boiling fraction boiling within the range of about 200-400° F., preparing a reforming charge stream blend consisting essentially of 1-20 volume 25 percent of said low boiling fraction, 50-90 volume percent of said intermediate boiling fraction, and 5-45 volume percent of said high boiling fraction, and subjecting said reforming charge stream blend to catalytic reforming to produce said gasoline. 30

3. A process for converting low octane naphtha to produce two motor gasolines having different research octane numbers and each of said gasolines having substantially balanced octane across the boiling range thereof, by distilling said naphtha into a light fraction boiling within 35 the range of about 90-200° F., an intermediate fraction boiling within the range of about 100° F.-300° F., and a heavy fraction boiling within the range of about 200-400° F., preparing a first catalytic reformer charge stream by blending portions of each of said fractions and sub-40jecting said first charge stream to catalytic reforming to produce a first motor gasoline having a balanced octane across the gasoline boiling range, and preparing a second catalytic reformer charge stream by blending portions of each of said fractions and subjecting said second 45 charge stream to catalytic reforming to produce a second motor gasoline having a research octane number below the research octane of said first gasoline and also having balanced octane across the gasoline boiling range.

4. The process of claim 3 wherein said first catalytic 50 reformer charge stream consists essentially of 1–10 volume percent of said light fraction, 60-80 volume percent of said intermediate fraction, and 15–35 volume percent of said heavy fraction; said second catalytic reformer charge consisting essentially of 10–30 volume percent of 55 said light fraction, 20–40 volume percent of said intermediate fraction, and 40–60 volume percent of said heavy fraction.

5. A process for converting low octane naphtha to produce two motor gasolines having different research octane numbers and each of said gasolines having substantially balanced octane across the boiling range thereof by 6

distilling said naphtha into a light fraction boiling within the range of about 90-200° F., an intermediate fraction boiling within the range of  $100-300^\circ$  F., and a heavy fraction boiling within the range of about 200-400° F., preparing a first catalytic reformer charge stream by blending portions of each of said fractions and subjecting said first charge stream to catalytic reforming at a severity above that required to produce about 90  $C_5$ + research octane to produce a first motor gasoline having a balanced octane across the gasoline boiling range, and preparing a second catalytic reformer charge stream by blending portions of each of said fractions and subjecting said second charge stream to catalytic reforming at a severity below that used in reforming said first charge stream to produce a second motor gasoline having a research octane number below the research octane of said first gasoline and balanced octane across the gasoline boiling range.

6. The process for converting low octane naphthas to gasoline, each of said gasolines having a substantially balanced octane throughout the gasoline boiling range, which process comprises separating isopentane from said naphtha for blending into said gasolines; fractionating the remainder of said naphtha into a light fraction boiling within the range of about 90-200° F., an intermediate fraction boiling within the range of about 100-300° F., and a heavy fraction boiling within the range of about 200-400° F.; preparing a first catalytic reforming charge stream and a second catalytic reforming charge stream, said first charge stream consisting essentially of 1-10 volume percent of said light fraction, 60-80 volume percent of said intermediate fraction, and 15-35 volume percent of said heavy fraction, and said second charge stream consisting essentially of 10-30 volume percent of said light fraction, 20-40 volume percent of said intermediate fraction and 40-60 volume percent of said heavy fraction; subjecting said first charge stream to catalytic reforming at a severity required to produce at least about 95 C5+ research octane number to produce a first reformate, and subjecting said second charge stream to catalytic reforming at a lower severity than that employed in reforming said first charge stream to produce a second reformate; blending a first portion of said isopentane with said first substantially balanced octane reformate to produce a premium gasoline having balanced octane throughout the gasoline boiling range, and blending a second portion of said isopentane with said second substantially balanced octane reformate to produce a regular gasoline having balanced octane throughout the gasoline boiling range.

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DELBERT E. GANTZ, Primary Examiner.

H. LEVINE, Assistant Examiner.