Nov. 7, 1967 L. E. DREHMAN ETAL 3,351,547

PROCESS FOR PRODUCING HIGH OCTANE GASOLINE

Filed Nov. 29, 1965 2 Sheets-Sheet 1

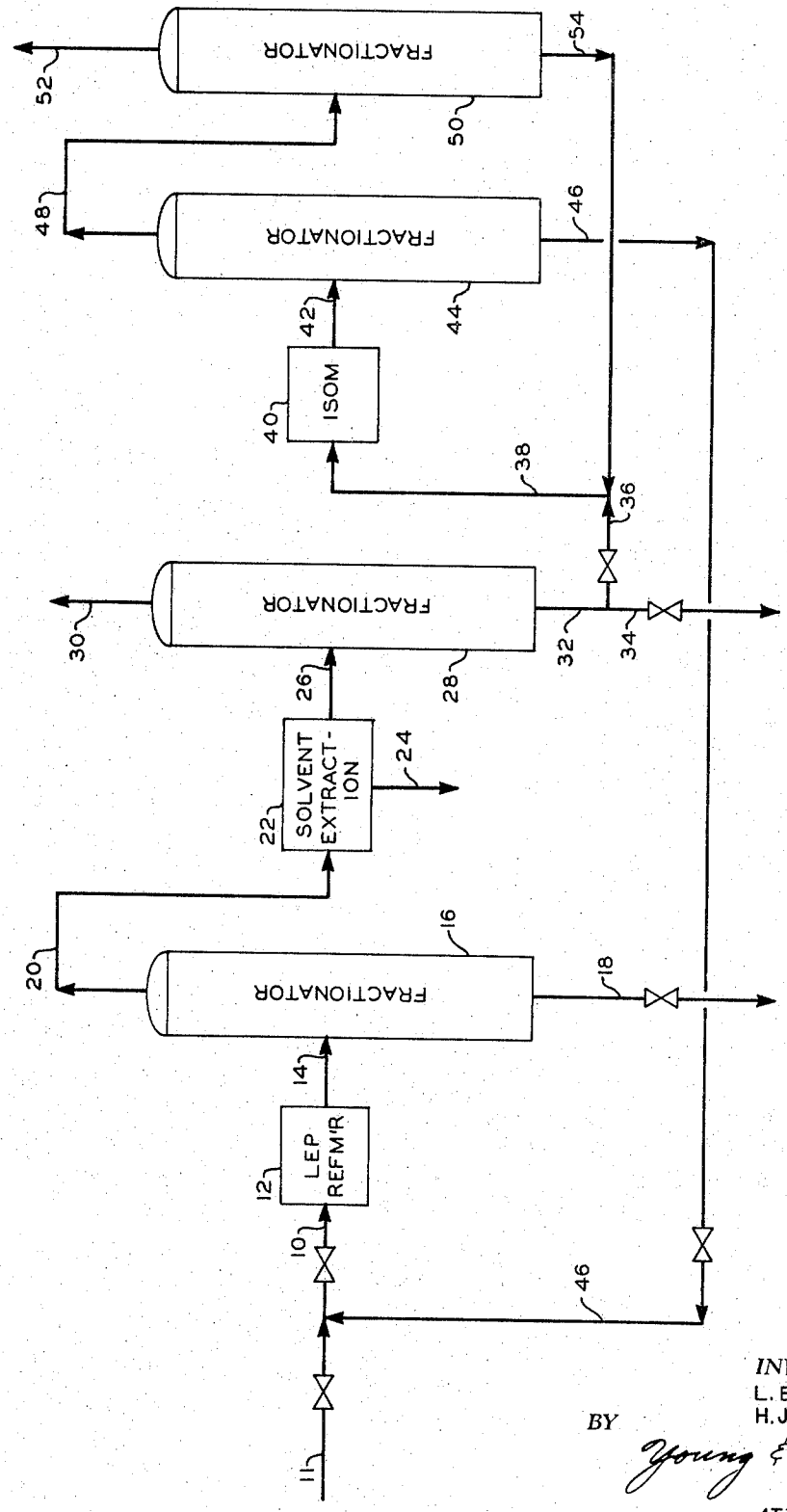


FIG. 1

INVENTORS
L. E. DREHMAN
H. J. HEPP

BY Young & Quigg

ATTORNEYS

Nov. 7, 1967 L. E. DREHMAN ETAL 3,351,547

PROCESS FOR PRODUCING HIGH OCTANE GASOLINE

Filed Nov. 29, 1965 2 Sheets-Sheet 2

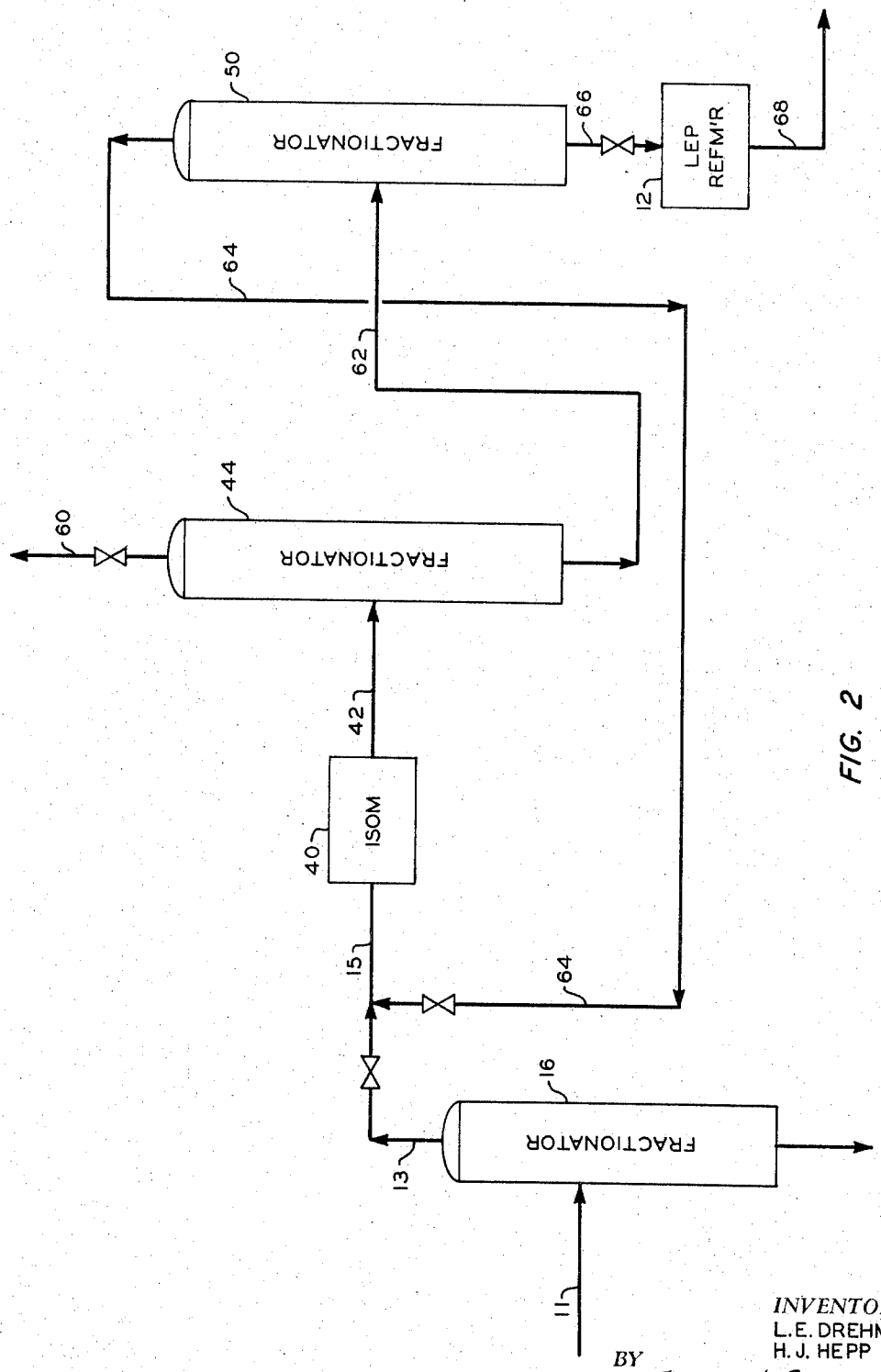


FIG. 2

INVENTORS
L.E. DREHMAN
H. J. HEPP

BY Young & Quigg

ATTORNEYS

United States Patent Office 3,351,547
Patented Nov. 7, 1967

3,351,547

PROCESS FOR PRODUCING HIGH OCTANE GASOLINE

Lewis E. Drehman and Harold J. Hepp, Bartlesville, Okla., assignors to Phillips Petroleum Company, a corporation of Delaware

Filed Nov. 29, 1965, Ser. No. 510,250
2 Claims. (Cl. 208—62)

This invention relates to a process for upgrading gasoline boiling range hydrocarbons to high octane motor fuel.

In one plant process, gasoline boiling range hydrocarbons (B.P. 175–300° F.) are upgraded to a motor fuel having a research octane number of 80 with 3 cc. of tetraethyl lead. The feed stream is reformed and fractionated to separate the C_8 and heavier hydrocarbons and the lighter fraction is solvent extracted with an alkylene glycol to recover aromatics and principally benzene as an extract stream and C_7 and lighter hydrocarbons, paraffinic and naphthenic hydrocarbons, as a raffinate stream, and the raffinate stream is fractionated to recover the C_7's as a bottoms fraction for motor fuel and a C_6 overhead fraction.

This invention is concerned with a process for further upgrading the stream of C_7 hydrocarbon bottoms fraction.

Accordingly, it is an object of the invention to provide an improved process for upgrading a stream of gasoline boiling range hydrocarbons to produce a high octane motor fuel. A further object is to provide a process for producing high octane motor fuel from a stream of gasoline boiling range hydrocarbons, which converts more of said hydrocarbons to high octane components than in present plant processes. Other objects of the invention will become apparent to one skilled in the art upon consideration of the accompanying disclosure.

The improved process of the invention comprises isomerizing the recovered C_7 stream of hydrocarbons downstream of the reforming and solvent extraction steps at relatively low temperature to form C_7 isomers of high octane value boiling below about 190° F., fractionating the isomerizate into a lighter fraction consisting principally of dimethylpentanes and other hydrocarbons boiling in the range of 175–190° F., an intermediate fraction boiling in the range of 190–205° F. containing the lower octane isomers, and a heavier fraction boiling above 205° F. The intermediate fraction is recycled to the isomerization step to isomerize the components thereof to higher octane isomers and the heavier fraction is recycled to the reforming step to convert the components thereof to the higher octane components of the lighter fraction obtained downsream of the isomerization zone.

In another embodiment of the process of the invention, non-reformed C_7 hydrocarbons are isomerized, and the isomerizate is fractionated into a lighter fraction consisting principally of dimethylpentanes and other hydrocarbons boiling in the range of 175–190° F., an intermediate fraction boiling in the range of 190–205° F. for recycle to the isomerization zone, and a heavier fraction boiling above 205° F. that is charged to the low-end-point reformer.

The invention is best illustrated and described with reference to the accompanying schematic drawing of which FIGURE 1 is a flow of a plant process in which gasoline boiling range hydrocarbons are upgraded to high octane motor fuel and FIGURE 2 is a flow of another embodiment of a portion of the plant process.

Referring to FIGURE 1, a feed stream of gasoline hydrocarbons boiling in the range of about 175 to 300° F. is fed thru line **10** to low-end-point reformer **12**. This low-end-point reformer is conventional in the art and

utilizes a catalyst such as platinum on alumina or other active reforming catalyst. The reformate is passed thru line **14** to a fractionator **16** where the C_8 and heavier hydrocarbons boiling above about 212 or 215° F. are recovered as a bottoms fraction thru line **18** and the lower boiling hydrocarbons (B.P. 120 to 212° F.) are recovered as an overhead fraction thru line **20**. The stream in line **18** is a motor fuel blending stock.

The overhead stream in line **20** consisting of C_7 and lighter hydrocarbons is passed to solvent extraction unit **22** where it is solvent extracted with an alkylene glycol, preferably diethyleneglycol or a diethylene glycol-triethylene glycol-water mixture, to recover an extract stream in line **24** comprising aromatics (principally benzene) and a raffinate stream in line **26** comprising principally C_7 and lower paraffins and naphthenes. The raffinate stream is passed from line **26** into a fractionator **28** wherein a separation is made to take the C_6 and lighter hydrocarbons overhead thru line **30** and the C_7 and higher boiling hydrocarbons in the bottoms stream thru line **32**. In fractionator **28** the cut point is about 180° F., the overhead fraction boiling in the range of 120–180° F., and the bottoms fraction boiling above 180° F. and consisting essentially of C_7 hydrocarbons.

Prior to the improvement of this invention, the C_7 stream in line **32** was recovered thru line **34** as a motor fuel having a research octane number of 80 with 3 cc. of TEL therein. In accordance with the invention, the C_7 stream in line **32** is passed thru lines **36** and **38** to isomerizing zone **40** where this stream is isomerized at relatively low temperatures in contact with a highly active isomerization catalyst to high octane isomers, particularly, those boiling at a temperature below 190° F. The isomerizing step is effected at temperatures not exceeding 350° F. such as in the range of 150–350° F. and preferably in the range of 200–350° F. A highly active isomerization catalyst such as acidic platinum-promoted alumina or silica-alumina or $AlCl_3$-HCl plus isobutane as an inhibitor, is used in the isomerization step. Another catalyst which is effective is a noble metal-boria-alumina composite. These catalysts are conventional in the art and need no further description. Pressure in the isomerization zone is maintained in the range of 50–1000 p.s.i.g. and preferably in the range of 200–600 p.s.i.g. Space velocity is maintained in the range of 0.5 to 10 weight of feed per hour per weight of catalyst. The isomerization may be effected in the presence of hydrogen and when used, an amount of hydrogen in the range of 0.01 to 15 moles, preferably 1 to 8 moles, per mole of feed is used. The isomerization step converts the feed stream to almost thermodynamic equilibrium composition at low temperatures (below about 350° F.) where dimethylpentanes are favored isomers.

The isomerizate is passed thru line **42** into fractionator **44** where a separation is made into a bottoms stream recovered thru line **46** and an overhead stream recovered thru line **48**. The heavier stream in line **46** comprising principally methylcyclohexane and normal heptane is recycled to line **10** as a portion of the feed to the low-end-point reformer **12**. The cut point in fractionator **44** is about 200° F., the overhead stream containing hydrocarbons boiling below 200° F. The lighter stream in line **48** comprising principally dimethylpentanes with lesser amounts of 2,2,3-trimethylbutane, cyclohexane, 1,1-dimethylcyclopentane, 2-methylhexane, 3-methylhexane, 1,3-dimethylcyclopentane and 1,2-dimethylcyclopentane, is passed into fractionator **50** for separation into an overhead stream recovered in line **52** boiling in the range of 175 to 190° F. and containing the lighter and higher octane C_7 isomers, particularly dimethylpentanes, and a heavier fraction recovered in line **54** and recycled to line **38** where it is mixed with the feed to isomerization zone

40 for conversion to desirable isomers. The stream recovered thru line 54 has a boiling range of 190 to 200° F. and contains the heavier dimethylpentanes of lower octane value and is the intermediate cut of the isomerizate in line 42.

Referring to FIGURE 2, corresponding elements and lines are correspondingly numbered. The main difference between the flow of this figure and the flow of FIGURE 1 is that C_7 isomerization and subsequent fractionation precedes rather than follows reforming. The fractionation downstream of isomerizer 40 is substantially and materially different from that in FIGURE 1 in that the lighter and higher octane hydrocarbons are recovered as overhead from fractionator 44 in line 60, the intermediate fraction is recovered as overhead from fractionator 50 thru line 64 and recycled to line 15 for mixing with the fresh feed in line 13 passing to the isomerization zone 40, and the heavier fraction is recovered as a bottoms stream from fractionator 50 in line 66. This bottoms stream is fed to the low-end-point reformer 12, or is optionally hydrodealkylated to yield mainly cyclohexane.

When operating with the arrangement illustrated in FIGURE 2, fractionator 44 is operated so as to make a cut at 190° F., the lower boiling hydrocarbons comprising the overhead stream in line 60 and the higher boiling hydrocarbons comprising the bottoms stream in line 62. Fractionator 50 is controlled so as to make a cut at about 205° F., recovering an intermediate fraction of the isomerizate boiling below 205° F. for recycle to the isomerization zone and a heavier fraction boiling above 205° F. as the stream in line 66 for recycling to the reformer.

The following examples illustrate different aspects of the invention and are not to be construed as unnecessarily limiting the invention.

TABLE I

Line No.	Volume b.p.d.		
	Before Invention	With Invention	Increase
10	10,550	12,100	1,550
14	9,060	10,410	1,350
18	4,250	4,780	530
20	4,810	5,630	820
24	470	470	0
30	940	940	0
32	3,400	4,220	820
34	3,400	0	−3,400
46	0	1,550	1,550
52	0	2,670	2,670
38	0	9,120	9,120
42	0	9,120	9,120
48	0	7,570	7,570
54	0	4,900	4,900

The above volumes demonstrate the effectiveness of the invention as compared to plant operation before the invention. The stream in line 52 is a high octane motor fuel having a RON+3 ml. TEL of 95+. There is also an increase in motor fuel blending stock in line 18. Thus, the invention upgrades a substantial part of the fuel stream in line 32 from 80 RON+3 ml. TEL to 95+RON+3 ml. TEL and increases the amount of blending fuel produced from 4250 to 4780 barrels per day.

EXAMPLE II

In utilizing the isomerization step and the recovery steps of FIGURE 2, 7000 barrels per day of a fresh feed consisting of a narrow-boiling range fuel comprising principally C_7 paraffins, naphthenes, and aromatics, are processed. This stream is separated from the 175–300° F. gasoline boiling range hydrocarbons by using fractionator 16 to separate a stream 13 having a boiling range

of about 175–235° F. from fresh feed stream 11. The volumes and stream compositions are set forth below:

TABLE II

Symbol	Stream No., Barrels/Day						
	13	15	64	42	60	62	66
A	35	35		2,525	2,525		
B		250	250	630	380	250	
C	155	250	95	195	100	95	
D	2,950	8,390	5,440	6,040	600	5,440	
E	85	150	65	65		65	
F	1,700	2,080	380	755		755	375
G	1,525	1,675	150	2,940		2,940	2,790
H	85	85		75		75	75
I	205	205		205		205	205
J	260	260					
	7,000	13,380	6,380	13,430	3,605	9,825	3,445

TABLE III

Symbol:	Boiling range, ° F.
A	175–180
B	187
C	190
D	193–198
E	200
F	209
G	211–214
H	218–221
I	224–229
J	231

The components represented by A include cyclohexane, 2,2-dimethylpentane, 2,4-dimethylpentane, and 2,2,3-trimethylbutane. B represents 3,3-dimethylpentane. C represents 1,1-dimethylcyclopentane. D includes 2,3-dimethylpentane, 2-methylhexane, 3-methylhexane, 1,3-dimethylcyclopentane, and trans-1,2-dimethylcyclopentane. E is 3-ethylpentane. F is normal heptane. G includes methylcyclohexane and cis-1,2-dimethylcyclopentane. H represents ethylcyclopentane and trimethylcyclopentanes. I represents dimethylhexanes and toluene is the J component.

The process illustrated in Example II produces a relatively pure methylcyclohexane concentrate. This stream in line 66 can be recycled to the reformer, as shown, to yield 3180 barrels per day of high octane gasoline (98 RON+3 ml. TEL). When the process is operated in this way the total yield of high octane gasoline is thus 6785 barrels per day, including stream 60. Alternatively, when cyclohexane is the desired product, the stream in line 66 can be hydrodealkylated to yield 1790 barrels per day of cyclohexane. The products other than cyclohexane from the hydrodealkylation are combined with stream 60 to yield 3900 barrels per day of high octane gasoline (98 RON+3 ml. TEL).

In another embodiment of the invention, the stream in line 42 of FIGURE 1 is subjected to the downstream separation (fractionation) steps of FIGURE 2. In this embodiment, stream 66 is fed to reformer 12, stream 64 is recycled to isomerization zone 40, and stream 60 is recovered as the high octane gasoline product.

Likewise, the stream in line 42 of FIGURE 2 may be fractionated in accordance with the fractionation illustrated in FIGURE 1.

The isomerization step is preferably operated at the lowest possible temperature since the final products, i.e., dimethylpentanes and methylcyclohexane are thermodynamically favored at low temperatures. Temperatures substantially below 350° F. are preferred. Another catalyst suitable for low temperature isomerization is the $HF+BF_3$ catalyst system.

Certain modifications of the invention will become apparent to those skilled in the art and the illustrative details disclosed are not to be construed as imposing unnecessary limitations on the invention.

We claim:

1. A process for upgrading a hydrocarbon stream consisting principally of a mixture of C_6–C_7 hydrocarbons including a substantial amount of n-heptane which comprises the steps of:

(1) reforming said mixture to produce an effluent stream containing paraffins, naphthenes, and aromatics including benzene;

(2) fractionating the effluent stream of step (1) to recover an overhead stream of principally C_7 and lighter hydrocarbons and a bottoms stream of principally C_8 and heavier hydrocarbons;

(3) solvent extracting the overhead stream of step (2) to recover an aromatic extract stream of principally benzene and a raffinate stream of principally paraffinic and naphthenic of C_6–C_7 hydrocarbons;

(4) fractionating the raffinate stream of step (3) to recover an overhead stream of principally C_6 hydrocarbons and a bottom stream of principally C_7 hydrocarbons including substantially all of the n-heptane in said raffinate stream;

(5) isomerizing the bottoms stream of step (4) at a temperature in the range of 200 to 350° F. to principally a stream of C_7 branched chain isomers;

(6) fractionating the isomerizate from step (5) into a lighter stream comprising hydrocarbons boiling below about 190° F. as a high octane motor fuel, an intermediate stream boiling in the range of about 190 to 200° F., and a heavier stream boiling above about 200° F.;

(7) recycling the heavier stream of step (6) to step (1); and

(8) recycling the intermediate stream of step (6) to step (5) to form higher octane isomers thereof.

2. The process of claim 1 wherein the feed stream in step (1) is a stream of 175–300° F. gasoline, the cut point in step (2) is about 212° F. and the cut point in step (4) is about 180° F.

References Cited

UNITED STATES PATENTS

2,947,683	8/1960	Hennig	208—65
3,001,927	9/1961	Gerhold et al.	208—64

DELBERT E. GANTZ, *Primary Examiner.*

ABRAHAM RIMENS, *Examiner.*