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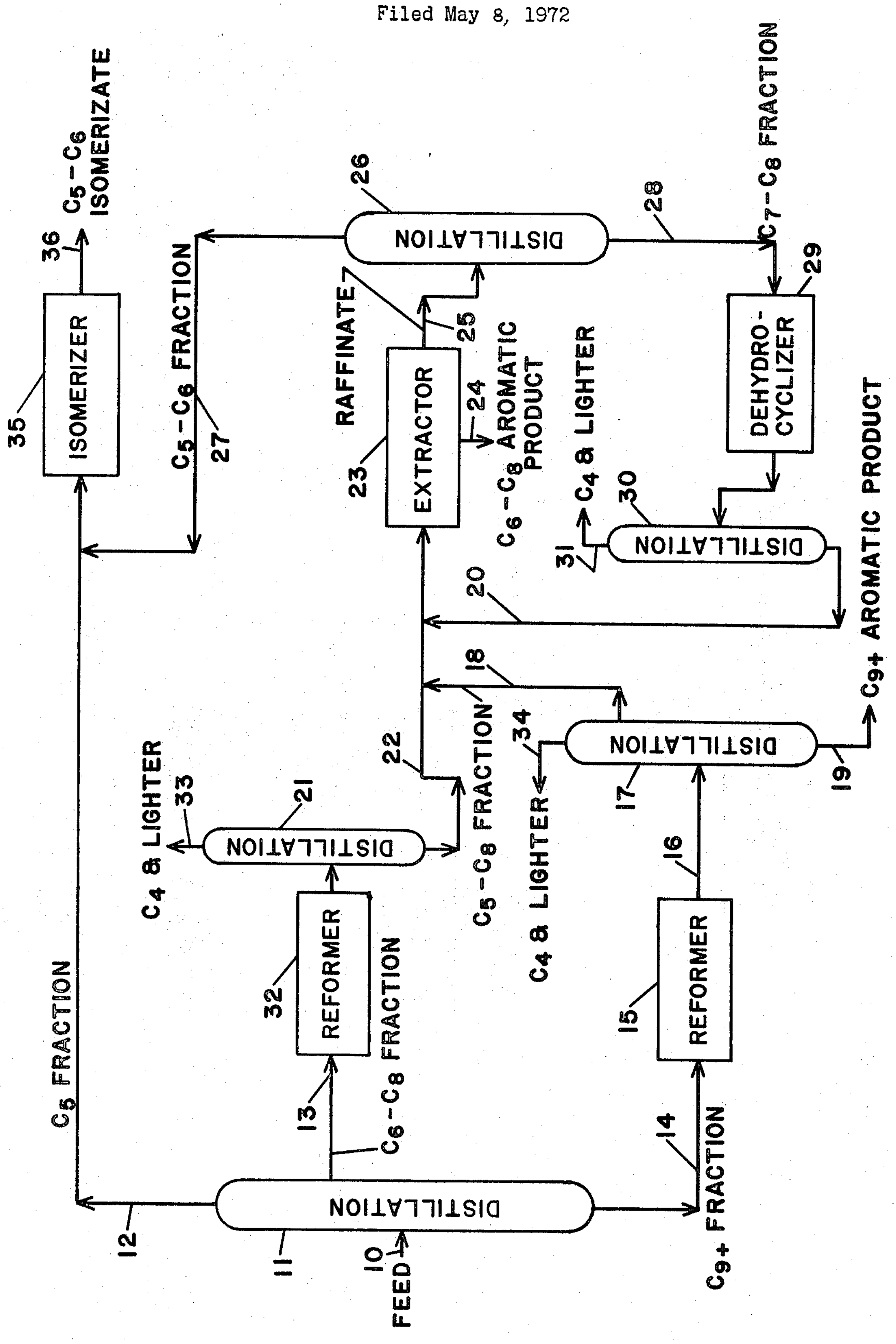

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UPGRADING WIDE RANGE GASOLINE STOCKS

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ABSTRACT OF THE DISCLOSURE

A process for upgrading wide range gasoline stocks is disclosed wherein the feed is separated into C_5, C_6–C_8 and C_{9^+} fractions, the C_6–C_8 and C_{9^+} fractions are separately reformed, reformate from the C_{9^+} fraction is distilled to remove C_5–C_8 material and yield a heavy aromatic product of high antiknock value, said C_5–C_8 material is combined with reformate from said C_6–C_8 fraction and with aromatic dehydrocyclizate from a subsequent step, the resulting mixture is extracted with an aromatic-selective solvent to yield a raffinate and C_6–C_8 aromatic product of high purity and antiknock value, the raffinate is distilled to obtain a C_5–C_6 paraffinic fraction and a heavy paraffinic fraction, the latter is catalytically dehydrocyclized to yield said aromatic dehydrocyclizate, the C_5–C_6 paraffinic fraction is combined with said C_5 fraction and the mixture is catalytically isomerized.

BACKGROUND OF THE INVENTION

This invention relates to a process involving a combination of refining steps for upgrading wide range gasoline stocks to fractions of higher antiknock values.

Numerous processes have been proposed heretofore for upgrading gasoline fractions by employing various combinations of refining steps such as distillation, reforming, dehydrocyclization, extraction and isomerization. The objective generally is to obtain products of good antiknock quality in high yields. Examples of such combination processes appear in the following U.S. patents: 2,891,902, H. V. Hess et al., issued June 23, 1959; 2,913,393, D. H. Sarno, issued Nov. 17, 1959; 2,921,015, R. N. Shiras, issued Jan. 12, 1960; 2,944,959, R. E. Kline et al., issued July 12, 1960; 2,967,143, M. F. Fontaine et al., issued Jan. 3, 1961.

SUMMARY OF THE INVENTION

The present invention provides a different processing procedure for upgrading wide range gasoline stocks involving a new combination of known types of refining steps. The process provides a way of securing an optimum yield-octane value relationship in upgrading the feed material to high quality blending stocks for motor fuel manufacture.

The process according to the invention involves the following combination of steps:

(a) Distilling a gasoline stock boiling mainly in the range of 90–400° F. to separate (1) a C_5 fraction, (2) a C_6–C_8 fraction boiling mainly in the range of 150–250° F. and (3) a residue boiling mainly in the range of 250–400° F.;

(b) Reforming said C_6–C_8 fraction in the presence of hydrogen and a platinum-containing reforming catalyst at temperatures and pressures in the respective ranges of 875–1000° F. and 150–700 p.s.i.g.;

(c) Separately reforming said residue in the presence of a platinum-containing reforming catalyst at temperatures and pressures in the respective ranges of 875–1000° F. and 150–700 p.s.i.g.;

(d) Distilling the reformate from step (c) to obtain a light reformate fraction boiling mainly in the range of 90–280° F. and to recover a heavy aromatic product of high antiknock value;

(e) Combining said 90—280° F. light reformate fraction with the reformate from step (b) and with aromatic dehydrocyclizate from step (g) infra and extracting the resulting mixture with an aromatic-selective solvent to obtain a raffinate and a light aromatic product of high antiknock value comprising C_6–C_8 aromatics;

(f) Distilling said raffinate to separate same into a C_5–C_6 light paraffinic fraction and a heavy paraffinic fraction boiling, respectively, mainly in the range of 90–165° F. and 165–280° F.;

(g) Reforming said heavy paraffinic fraction from step (f) under catalytic dehydrocyclizing conditions to remove hydrogen therefrom and produce an aromatic dehydrocyclizate for use as specified in step (e);

(h) Combining said C_5–C_6 light paraffinic fraction from step (f) with said C_5 fraction from step (a) and subjecting the mixture to catalytic isomerization conditions to yield C_5–C_6 isoparaffins.

BRIEF DESCRIPTION OF DRAWING

The invention is described in conjunction with the accompanying drawing which is a schematic flowsheet depicting the sequence of steps of the process.

DESCRIPTION

The feedstock for the present process is a wide range, debutanized gasoline fraction including C_5 paraffins and boiling mainly in the range of 90–400° F. The invention is most useful for the processing of straight run gasoline stocks but other stocks, such as naphthas from catalytic or thermal cracking, may be included if desired. The process converts the feedstock into three products: (1) a C_5–C_6 paraffinic isomerizate; (2) a C_6–C_8 aromatic product of high purity typically having F–1 octane rating in the range of 110–115; and (3) a heavy aromatic product (C_{9^+}) typically having F–1 octane rating of 105–107. These products can be blended in any desired way with each other and/or with other gasoline components to produce motor fuels of high antiknock value.

With reference to the accompanying drawing, the debutanized feed is introduced through line **10** to a distillation column **11** which fractionates it into three streams. The overhead stream obtained through line **12** is a C_5 fraction which boils below 150° F. A C_6–C_8 fraction that boils mainly in the range of 150–250° F. is obtained as a sidestream via line **13**. The residue, which is removed through line **14**, is a C_{9^+} fraction boiling mainly in the range of 250–400° F.

The C_{9^+} residue fraction is passed through line **14** to a reforming operation, illustrated schematically by reformer **15**, wherein it is subjected to catalytic hydroforming. The reforming reaction is carried out by means of a platinum-containing reforming catalyst in the presence of hydrogen at suitable reforming temperatures in the range of 875–1000° F. and pressures of from 150 to 700 p.s.i.g., preferably 300–500 p.s.i.g. A weight hourly space velocity (WHSV) generally in the range of 0.5–10 weights per hour per weight of catalyst is utilized, with preferred WHSV generally being 1–3. Average inlet temperatures to the reformer reactors usually are in the range of 900–1000° F. A plurality of reactors in series generally is used in this type of operation, with a heater ahead of each reactor for heating the reformer feed to the desired temperature and reheating the hydrocarbon reactants to compensate for reductions in temperature that occur due to the endothermic reactions which take place. Under these reforming conditions naphthenes dehydrogenate to aromatics and a considerable portion of the C_9 and heavier material is converted to C_5–C_8 products due to the dealkylation and cracking reactions that occur. These C_5–C_8 products include both aromatic and saturated hydrocarbon components.

The effluent from reformer **15** is withdrawn through line **16** and conventionally is passed through a cooler and gas-liquid separator (not shown) so that the hydrogen-containing gas phase can be recycled. A hydrogen recycle rate typically in the range of 3000–9000 s.c.f./bbl. of reformer feed is used and the hydrogen content of the recycle stream is generally in the range of 60–98% by volume.

An of the known or conventional platinum-containing reforming catalysts can be used for effecting the hydroforming reaction in reformer **15**. Such catalysts have been described in numerous prior art references and need not be described herein. Reference can be made, for example, to the following: Catalytic Processes and Proven Catalysts by C. L. Thomas, pp. 54–57, Academic Press (1970); U.S. Pat. 2,479,109, V. Haensel, issued Aug. 16, 1949; and U.S. Pat. 2,478,916, V. Haensel et al., issued Aug. 16, 1949. The platinum-containing catalyst can also contain other metals, such as rhenium, ruthenium, rhodium or iridium, which are beneficial. The platinum-rhenium reforming catalysts are particularly desirable and such catalysts have been described in U.S. Pat. 3,415,737, H. E. Kluksdohl, issued Dec. 10, 1968 and U.S. Pat. 3,434,960, R. L. Jacobsenson, issued Mar. 25, 1969. Platinum-iridium reforming catalysts are disclosed in U.S. Pat. 3,554,902, W. C. Buss, issued Jan. 12, 1971.

The liquid reformate from the above-described reforming operation is debutanized and the normally liquid portion is separated into two fractions, all as indicated schematically by distillation zone **17**. The C_4 and lighter products are removed from the system via line **34**. The light reformate fraction composed of the C_5–C_8 hydrocarbons and boiling mainly in the range of 90–280° F. is separately recovered from zone **17** through line **18** for further processing as described below. The heavy reformate stream is obtained as bottoms through line **19** and is removed from the system as one of the desired products. This product is highly aromatic, typically containing 85–90% aromatic components and having F–1 clear octane rating of 105–107.

The C_6–C_8 stream obtained from column **11** passes through line **13** and is sent to another reforming zone **32**. This reformer also utilizes a platinum-containing catalyst and can be operated at substantially the same conditions as described for reformer **15**, with temperatures and pressures in the ranges of 875–1000° F. and 150–700 p.s.i.g., respectively, and WHSV in the range of 0.5–10. A preferred pressure range is 250–400 p.s.i.g., WHSV preferably is 1–3 and inlet temperatures to the reactors generally are in the range of 900–1000° F.

The liquid reformate obtained from the gas-liquid separator (not shown) after reformer **32** is debutanized in column **21** and the C_4 and ligher components are removed from the system via line **33**. Debutanized reformate, which is obtained through line **22** and which boils mainly in the range of 90–280° F., is combined with the C_5–C_8 fraction from line **18** and with dehydrocyclizate derived as hereinafter described through line **20**, both of which latter materials also have about this same boiling range. The mixture is then treated in an extraction unit, schematically illustrated by extractor **23**, wherein it is countercurrently extracted with an aromatic-selective solvent in order to separate the aromatic from non-aromatic components. Procedures for carrying out the selective extraction of aromatics from C_6–C_8 naphtha stocks are well known and need not be described in detail here. The Udex process which utilizes a glycol type solvent has had wide commercial use for selectively extracting C_6–C_8 aromatics and is a preferred way of carrying out the operation represented by extractor **23**. This process is described in Hydrocarbon Processing, September 1970, p. 248. Upon recovery of the extract from the solvent phase, a C_6–C_8 aromatic product of high purity is obtained and is removed through line **24** as another product of the present process. This product has a boiling range of about 175–280° F., consists essentially of benzene, toluene and xylenes, and typically has F–1 clear octane number in the range of 110–115. It can be used as a blending stock for high antiknock value gasoline or optionally can be fractionally distilled to recover the individual aromatics as industrial chemical products.

The raffinate from extractor **23** passes through line **25** to distillation zone **26** wherein it is separated into a C_5–C_6 overhead fraction obtained through line **27** and a C_7–C_8 bottoms fraction withdrawn through line **28**. These fractions are both highly paraffinic and their respective boiling ranges are about 90–165° F. and 165–280° F.

The C_7–C_8 paraffinic fraction is sent from line **28** to a dehydrocyclization step illustrated by dehydrocyclizer **29**. This is a hydroformer which can be operated under conditions much like those utilized in reformers **15** and **32**. Dehydrocyclization of the paraffin feed to this step can be carried out by any suitable reforming catalyst, such as a chromia-alumina catalyst, a molybdena-alumina catalyst, or a platinum-containing reforming catalyst as referred to with reference to the operation of reformers **15** and **32**. As a general rule, the pressure level is somewhat lower for the dehydrocyclization step than for either of these reforming steps. Inlet temperatures to dehydrocyclizer **29** usually are in the range of 900–1000° F., while the pressure generally is below 500 p.s.i.g. and usually falls within the range of 50–300 p.s.i.g. Suitable reforming conditions for dehydrocyclizing straight chain hydrocarbons are described in the prior art, e.g. in the following U.S. patents: 2,886,508, H. V. Hess et al., issued May 12, 1959 and 2,944,001, C. N. Kimberlin, Jr. et al., issued July 5, 1960. Under the dehydrocyclizing conditions maintained in hydroformer **29** the paraffinic hydrocarbons undergo dehydrogenation and cyclization, as a result of which a reformate or dehydrocyclizate product with a substantial aromatic content is obtained.

The effluent from dehydrocyclizer **29** passes through a cooler and gas-liquid separator (not shown) and the liquid product then goes to debutanizer column **30** from which the C_4 and lighter components are removed via line **31**. The debutanized dehydrocyclizate obtained from the bottom of column **30** through line **20** boils mainly in the range of 90–280° F. and is recycled to line **22** to become a component of the feed to extractor **23**.

The C_5 fraction obtained from column **11** (line **12**) is admixed with the C_5–C_6 paraffinic fraction from column **26** (line **27**) and the mixture is subjected to isomerization as illustrated by isomerizer **35**. Numerous procedures have been described in the prior art for isomerizing C_5–C_6 paraffins and any of them can be used for the present isomerization step. Descriptions of such procedures are given in an article entitled "Advances in Isomerization" by P. A. Lawrence et al., Proceeding of Seventh World Petroleum Congress, vol. IV, pp. 135–145, Elsevier Publishing Co. (1967). Other examples of processes for isomerizing such paraffins appear in the following U.S. patents: 2,834,823, J. L. Patton et al., issued May 13, 1958; 3,527,835, H. A. Benesi, issued Sept. 8, 1970; 3,577,479 and 3,578,725, D. E. Jost et al., issued May 4 and 9, 1971, respectively.

The isomerizate obtained from isomerizer **35** through line **36** is composed of C_5–C_6 paraffins with a higher isoparaffin content than the feed to this step. The isomerizate has F–1 antiknock value typically in the range of 80–90 and can be withdrawn as the other product of the process. Optionally it can be treated to separate n-paraffins from the isoparaffins, e.g. by means of zeolitic molecular sieves as disclosed in U.S. Pat. 2,888,394, E. R. Christensen et al., issued May 26, 1959, and the separated n-paraffins can be recycled to isomerizer **35** for further conversion.

The following is a specific illustration of the present process based on feeding 100 vols./hr. of straight run gasoline boiling 90–400° F. and containing about 12% aromatics, 31% naphthenes and 57% paraffins:

The feed is fractionated in column **10** to give 10 vols. of C_5 fraction (line **12**) which is essentially all paraffins, 40 vols. of C_6–C_8 fraction (line **13**) which is about 10% aromatics, 35% naphthenes and 55% paraffins, and 50 vols. of residue (line **14**) which is about 15% aromatics, 35% naphthenes and 50% paraffins. Reforming of the residue in reformer **15**, using reactor inlet temperatures of 925–975° F., pressure of about 400 p.s.i.g., WHSV of about 2 and hydrogen recycle rate of about 6000 s.c.f./bbl., followed by fractionation (column **17**) gives about 20 vols. of C_5–C_8 reformate (line **18**) and 20 vols. of C_{9+} aromatic product (line **19**). The C_5–C_8 reformate contains about 3% benzene, 12% toluene and 25% xylenes, the remainder being largely paraffins. The C_{9+} product contains about 90% aromatics and has F–1 clear octane number of about 106.

Reforming of the 40 vols. of C_6–C_8 fraction in reformer **32**, employing about the same conditions as in reformer **15** except a somewhat lower pressure of about 325 p.s.i.g. and a hydrogen recycle rate of about 4000 s.c.f./bbl., followed by debutanization (column **21**) yields 32 vols. of C_5–C_8 reformate (line **22**) containing about 6% benzene, 17% toluene and 17% xylenes. This reformate is combined with the other C_5–C_8 reformate (line **18**) and with 23 volumes of dehydrocyclizate (line **20**) to give 75 vols. of feed of extractor **23**. The C_6–C_8 extract product (line **24**) amounts to 28 vols. composed of about 12% benzene, 42% toluene and 46% xylenes. The raffinate (line **25**) amounting to 47 vols. is distilled (column **26**), giving 16 volts. of C_5–C_6 paraffinic fraction (line **27**) and 31 vols. of C_7–C_8 paraffinic fraction (line **28**) which latter is fed to dehydrocyclizer **29**. This step employs a platinum-containing reforming catalyst, reactor inlet temperatures in the range of 925–975° F., pressure of about 175 p.s.i.g., WHSV of 2, and a hydrogen recycle rate of the order of 6000 s.c.f./bbl. Upon debutanization (column **30**) of the reactor product, 23 vols. of C_5–C_8 dehydrocyclizate are obtained (line **20**) having individual aromatic contents of 4% benzene, 23% toluene and 24% xylenes.

The 10 vols. of C_5 fraction (line **12**) are combined with the 16 vols. of C_5–C_6 paraffinic fraction (line **27**) and the mixture is hydroisomerized (isomerizer **35**) in vapor phase using a highly chlorided platinum-on-alumina catalyst, temperature of about 300° F., pressure of about 1000 p.s.i.g., WHSV of 2, and a hydrogen recycle rate of about 3000 s.c.f./bbl. This results in about 25 vols. of C_5–C_6 isomerizate having F–1 clear octane value of about 83.

The invention claimed is:

1. Process for upgrading a wide range gasoline stock which comprises:

(a) distilling a gasoline stock boiling mainly in the range of 90–400°F. to separate (1) a C_5 fraction, (2) a C_6–C_8 fraction boiling mainly in the range of 150–250° F. and (3) a residue boiling mainly in the range of 250–400° F.;

(b) reforming said C_6–C_8 fraction in the presence of hydrogen and a platinum-containing reforming catalyst at temperatures and pressures in the respective ranges of 875–1000° F. and 150–700 p.s.i.g.;

(c) separately reforming said residue in the presence of a platinum-containing reforming catalyst at temperatures and pressures in the respective ranges of 875–1000° F. and 150–700 p.s.i.g.;

(d) distilling the reformate from step (c) to obtain a light reformate fraction boiling mainly in the range of 90–280° F. and to recover a heavy aromatic product of high antiknock value;

(e) combining said 90–280° F. light reformate fraction with the reformate from step (b) and with aromatic dehydrocyclizate from step (g) infra and extracting the resulting mixture with an aromatic-selective solvent to obtain a raffinate and a light aromatic product of high antiknock value comprising C_6–C_8 aromatics;

(f) distilling said raffinate to separate same into a C_5–C_6 light paraffinic fraction and a heavy paraffinic fraction boiling, respectively, mainly in the ranges of 90–165°F. and 165–280° F.

(g) reforming said heavy paraffinic fraction from step (f) under catalytic dehydrocyclizing conditions to remove hydrogen therefrom and product an aromatic dehydrocyclizate for use as specified in step (e);

(h) combining said C_5–C_6 light paraffinic fraction from step (f) with said C_5 fraction from step (a) and subjecting the mixture to catalytic isomerization conditions to yield C_5–C_6 isoparaffins.

2. Process according to claim **1** wherein step (g) is carried out at temperatures in the range of 900–1000° F. and pressures below 500 p.s.i.g.

3. Process according to claim **2** wherein steps (b), (c) and (g) are carried out a pressures, respectively, in the ranges of 250–400 p.s.i.g., 300–500 p.s.i.g., and 50–300 p.s.i.g.

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