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2,939,834

FRACTIONATION AND ABSORPTION PROCESS

Filed Aug. 26, 1957

2 Sheets-Sheet 1

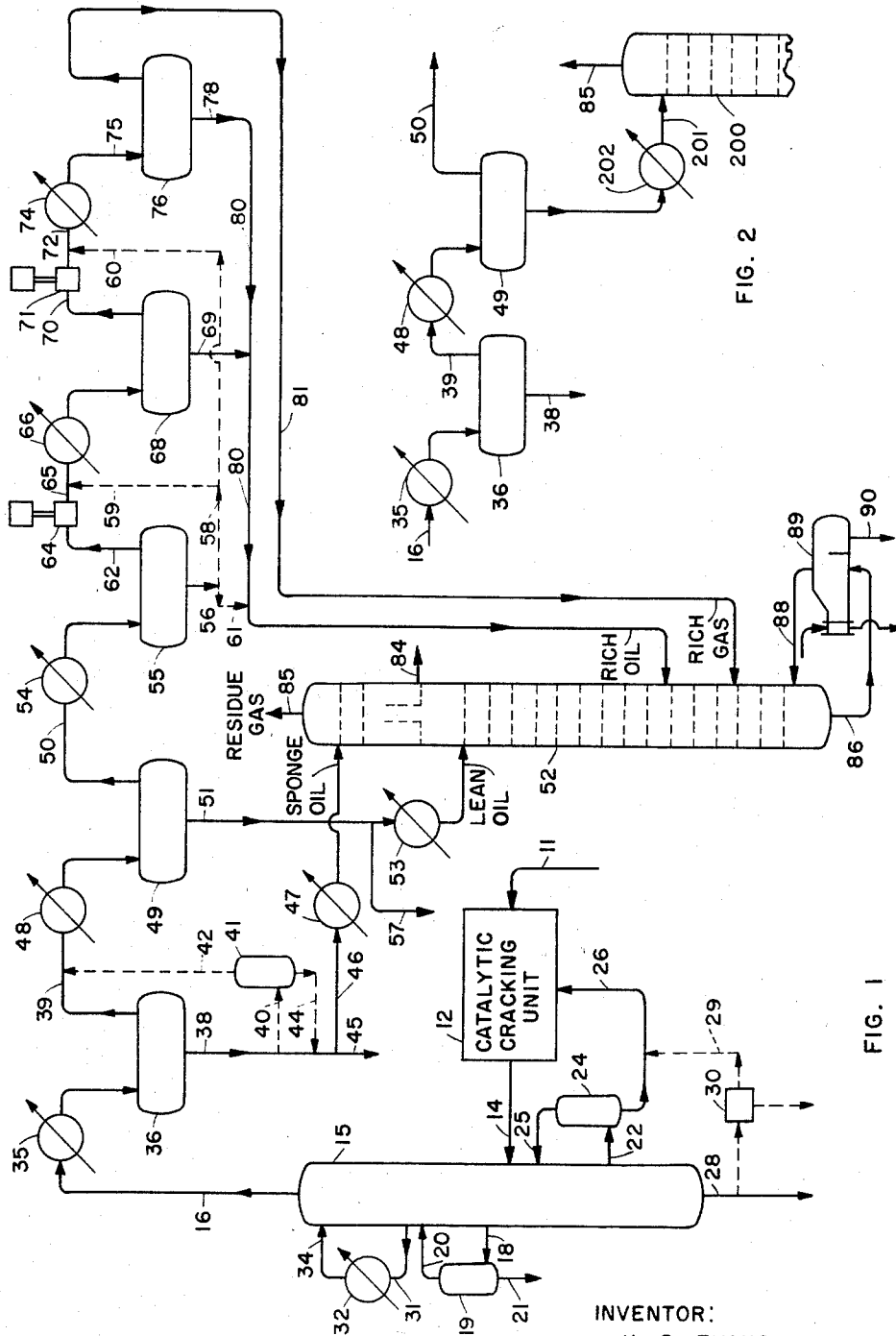


FIG. 1

FIG. 2

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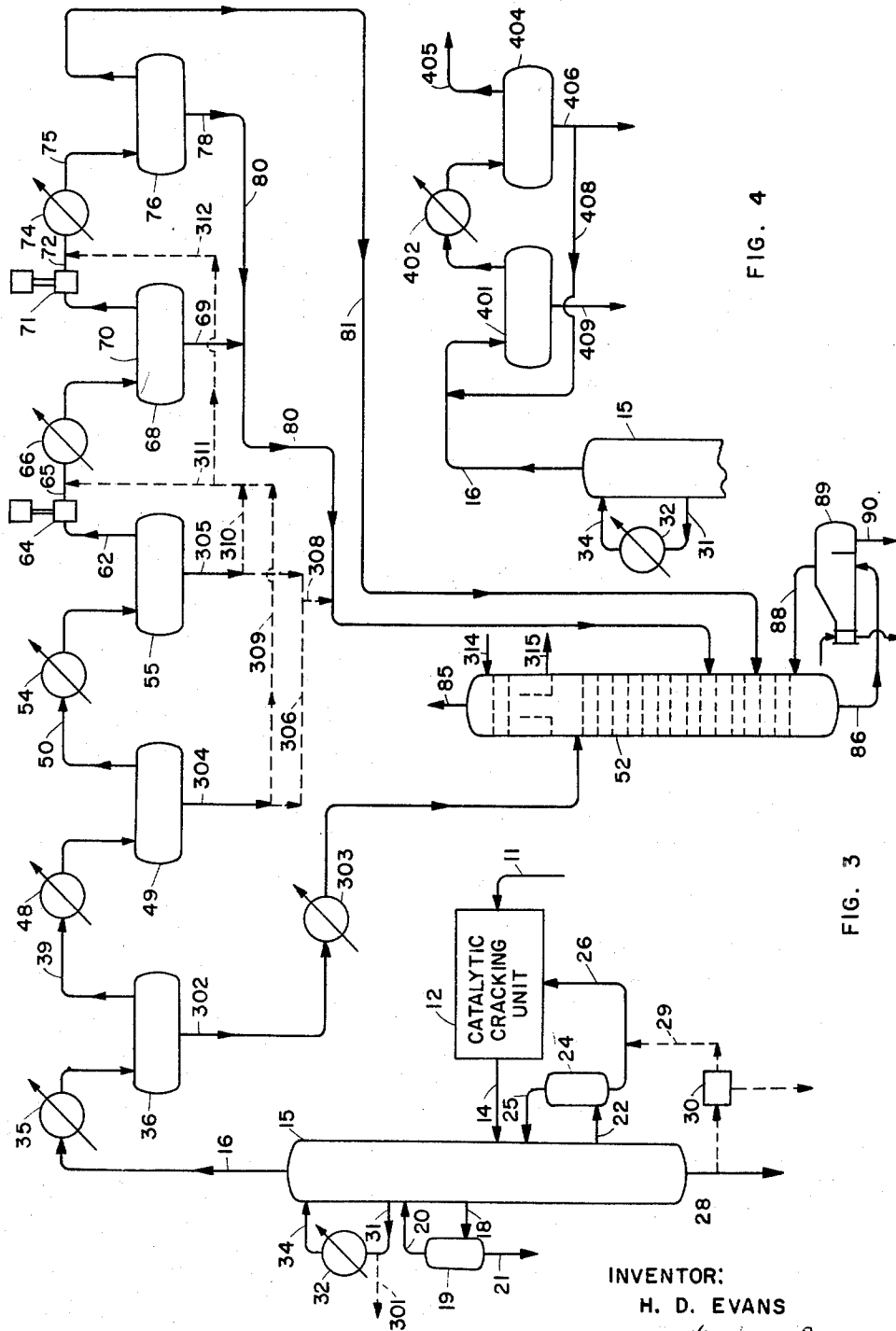


FIG. 4

Fig. 3

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1

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FRACTIONATION AND ABSORPTION PROCESS

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8 Claims. (Cl. 208—101)

This invention relates to an improved method for the recovery of gasoline and lighter hydrocarbons from catalytically cracked oils.

It is an object of this invention to provide an improved process for the recovery of gasoline and light hydrocarbons from catalytically cracked oils. It is a further object to provide an improved method for recovering a cracked gasoline of higher octane number and lower end point from the overhead vapors of the cracking product fractionator comprising heavy naphtha and lighter fractions. It is a further object to provide a simple method for producing a lean oil for use in rectified absorption of light hydrocarbons produced in catalytic cracking.

Briefly stated, this invention is an improved process for recovering gasoline and lighter hydrocarbons from the products of a catalytic cracking unit. It comprises taking as overhead from the cracked products fractionator a vapor stream comprising all gasoline and lighter components and, optionally, heavy naphtha; partially condensing the vapor stream in stages to produce partial condensates including a heavy gasoline which is used at least in part as absorber oil in a rectified absorber; compressing the remaining vapors; and contacting the light gasoline, compressed vapors and liquid compressor condensate with the heavy gasoline in the rectified absorber to recover a rich oil containing the cracked gasoline components and recovered light hydrocarbons. This rich oil can then be stabilized in the conventional manner to produce stable gasoline and C₃ and C₄ hydrocarbon fractions.

The process of this invention has a number of advantages over the conventional methods of recovering products from the catalytic cracking of petroleum fractions. It adds flexibility to the gasoline recovery system by permitting the production of several gasoline streams of selected properties without requiring more than the usual amount of fractionating and associated equipment. This invention provides the further advantage that the pressure drop in the fractionator condensers is reduced and the heat transfer coefficient may be increased by reducing liquid flow through the condensers. The invention permits the direct production from the fractionator overhead of an oil which is suitable as sponge oil in the rectified absorber without further separate treatment.

The preferred modification of this invention provides a further substantial advantage in that less total heat exchange area is required to produce a gasoline of lower end point and a separate heavy naphtha fraction. This is true by virtue of the fact that the overhead from the fractionating column is at a higher temperature than obtains conventionally, so that the temperature differential in the overhead heat exchangers is larger and heat exchange is more efficient. In the same modification the segregation of a heavy low octane naphtha fraction from the catalytically cracked gasoline is possible without affecting the flows in the fractionator itself. It permits the production of a catalytically cracked gasoline of lower

2

end point, with a given fractionator, than would be conventionally possible without overloading the top section of the fractionator. Other advantages of the process of this invention will be apparent to those skilled in the art.

The invention will be better understood and further objects of the invention will appear from the following description which is made with reference in part to the accompanying drawing wherein:

Fig. 1 is a simplified flow sheet illustrating the preferred mode of practicing the invention;

Fig. 2 is a partial flow sheet illustrating a modification of the preferred mode of practicing the invention;

Fig. 3 is a flow sheet illustrating a further mode of practicing the invention; and

Fig. 4 is a partial flow sheet illustrating a further modification of the invention.

In the following description the same numerals are used in different figures to identify the identical equipment and lines. Auxiliary equipment such as pumps, valves, instrumentation and the like is not shown, to simplify the description. The proper location of such equipment will be evident to those skilled in the art.

The present invention is concerned with an improved method of processing the heavy naphtha, gasoline and light hydrocarbons produced in a conventional catalytic cracking operation. In Figs. 1 and 3 a typical cracking feed such as a straight run heavy gas oil or reduced crude is charged through line 11 to catalytic cracking unit 12 which may be any conventional unit such as a fixed bed type, a moving bed type, e.g., a thermofor unit, or a fluid type, all of which are well known to the art.

The total cracked product stream passes from the unit through line 14 to fractionator 15 in which the cracked product is separated into fractions of different boiling ranges. Conventionally, there is withdrawn from this column a vapor overhead stream comprising gasoline and lighter hydrocarbons and sometimes comprising a heavy naphtha fraction as well; a light gas oil side stream; a heavy gas oil side stream which may be recycled to the cracking step; and a bottoms stream, which may also be recycled to the cracking step. As illustrated, an overhead vapor stream is withdrawn through line 16. A light gas oil stream is withdrawn through line 18 and stripped in stripper 19 from which the overhead vapors are returned to the column via line 20 and the stripped light gas oil is withdrawn via line 21. The heavy gas oil fraction is withdrawn through line 22 and stripped in stripper 24 from which the vapors are returned to the column through line 25 and the stripped heavy gas oil recycled to the cracking unit through line 26. The bottoms fraction is withdrawn through line 28 and may be taken for other uses or may be returned through line 29. When unit 12 is of the fluid type, line 29 contains settler 30 which removes entrained catalyst. The fraction returned through line 29 to a fluid type cracking unit is generally known as slurry oil. Cooling of the top section of the column is provided by withdrawing an internal reflux fraction through line 31, cooling it in heat exchanger 32 and returning it to the column through line 34 or by returning a portion of the condensed top vapors as reflux.

The system just described is a conventional method of catalytic cracking and distillation of cracking product. Conventionally, the overhead vapors withdrawn from the column are condensed by passing them through several large condensers in series or series-parallel and withdrawing the total condensate into a liquid accumulator drum from which the uncondensed vapors are then passed to a compressor system in which further liquid is produced by compression and cooling. The first-mentioned condensate is known as low pressure distillate and the

condensate produced after compression is known as compressor condensate. At least the compressor condensate and the uncondensed compressed gases are charged to an absorption system in which there is produced an unstabilized gasoline and a lean gas from which essentially all products having three or more carbon atoms per molecule are removed. The gasoline is subsequently stabilized.

It is known to carry out the absorption in a so-called rectified absorber or fractionating absorber in which a liquid and/or vapor fraction containing the light hydrocarbon components to be recovered is passed into the lower section of the absorber where it flows counter-currently to a so-called lean oil, which is generally a stabilized gasoline taken from the debutanizer. The gasoline absorbs the lighter components and passes out of the bottom of the column while the lean gas passes out of the top. It is also known to pass into the top section of the rectified absorber a sponge oil, generally a heavy naphtha fraction or light gas oil, which serves to absorb further propane, butane and gasoline components carried in the lean gas stream and which is generally withdrawn from the column from a drawoff plate above the lean oil feed plate.

The present invention provides an improved method for recovering catalytically cracked gasoline and light hydrocarbon components from a system comprising a fractionator and a rectified absorber of the type described.

The preferred method of operating the process of this invention is illustrated by Fig. 1. In this method the overhead vapor stream from fractionator 15 consists of heavy naphtha and lighter fractions. The ASTM distillation end point of the heavy naphtha present in this stream is in the range from 440°–500° F. Heavy naphtha is generally considered to be that fraction boiling between the end point of gasoline and a temperature in the stated range. Although the final boiling point of conventional gasoline may be as high as 425° F., it has been found that the octane number of the heaviest components of catalytically cracked gasoline is particularly low and that these components dilute the crankcase oil in internal combustion engines. Therefore it is desirable to eliminate these components from the gasoline fraction in order to improve its quality. It is a particular advantage of this invention, especially when operating in accordance with Fig. 1, that a simple method is provided for producing a catalytically cracked gasoline of improved octane number, having an end point between 350° and 400° F., although gasoline with an end point of 425° F. or higher may be produced, if desired.

The fractionator overhead vapors in line 16 are partially condensed in condenser 35 which is suitably of the conventional, water-cooled heat exchanger type. The amount of condensation obtained in condenser 35 is a function of the heat exchanger surface available, the entering and exit temperature of the cooling water thereto, and the rate of vapor flow as well as of other known factors. The proportion of the total vapors which is condensed is controlled in a manner well known to the chemical engineer, e.g., by controlling the rate and temperature of cooling water, to condense the heaviest fraction of the vapors boiling mainly in the range from the desired end point of gasoline to the end point of heavy naphtha. Typically the fraction condensed has a 10% ASTM boiling point of about 300° to 350° F., and a final boiling point of about 440°–480° F. This liquid may contain from 30 to 50%, of gasoline boiling range components but contains no lighter hydrocarbons. The gasoline content of this stream represents only a small portion of the total gasoline in the fractionator overhead, and comprises the undesirable heaviest gasoline components. The effluent from condenser 35 is separated into a liquid and a vapor fraction in separator or accumulator 36. The liquid is removed through line 38. In an optional operation, indicated by dashed lines, this liquid may be passed through line 40 to stripper 41 in

which the gasoline components are taken overhead through line 42 for recombination with the vapor from separator 36 while the stripped liquid, now essentially a heavy naphtha, is returned to line 38 via line 44. The liquid in line 38 may be discarded from the system through line 45 for further workup in a known manner. For example, heavy cracked naphtha may be further converted by such a process as thermal reforming to produce additional gasoline components. Alternatively, all or part of the liquid in line 38 may be passed through line 46 containing cooler 47 to be used as sponge oil in the rectified absorber 52, described below.

The vapors from the first separator 36 pass through line 39 to a second condenser 48 in which a further fraction is condensed. Condenser 48 is similar or identical to condenser 35. Conditions therein are controlled to condense a fraction comprising essentially the heavier portion of the gasoline boiling range components of the cracked product. The fraction suitably has a 10% point between 200° and 250° F. and a final boiling point between 350° and 425° F., preferably in the lower part of that range; it is substantially free of components boiling in the heavy naphtha boiling range. The effluent from condenser 48 is separated into a liquid and a vapor fraction in separator or accumulator 49. The liquid from accumulator 49 passes through line 51 containing cooler 53 to rectified absorber 52 in which it is used as lean oil. A portion of the heavy gasoline fraction may be withdrawn through line 57 to be blended directly into motor gasoline or to be further upgraded, e.g., by catalytic reforming.

The vapors from accumulator 49 pass through line 50 to condenser 54, which is of the same type as condensers 35 and 48. In condenser 54 the remaining portion of the vapors is condensed which is condensable at cooling water temperature at the low pressure in the range from 2 to 10 p.s.i.g. which prevails in this part of the system. The condenser effluent passes to separator or accumulator 55. The liquid fraction from accumulator 55 consists of the lighter gasoline components and some normally gaseous hydrocarbons, i.e., pentanes, butanes, propane and the corresponding olefins. The liquid fraction is withdrawn from accumulator 55 through line 56 and may be disposed of in either of two ways. It may be used as compressor sponge oil by passage through lines 58, 59 and 60 or it may be passed directly to the rectified absorber through lines 61 and 80. In any event, the liquid fraction from accumulator 55 is ultimately passed to absorber 52, in which the lightest gaseous components are removed overhead as residue gas and the remaining gasoline and desired lighter components are taken as bottoms.

The uncondensed vapors from accumulator 55 are passed through line 62 to compressor 64, in which they are compressed from a pressure in the range between 2 and 10 p.s.i.g. to a higher pressure in the range between 50 and 100 p.s.i.g. The compressed vapors pass through line 65 to cooler or interstage condenser 66, which may be a conventional water cooled heat exchanger. If desired, compressor sponge oil is added to line 65 through line 59. The effluent from cooler 66 passes to separator or accumulator 68 in which a liquid interstage condensate fraction is removed through line 69 while the vapor fraction passes through line 70 to second compressor stage 71 in which the gases are further compressed to a pressure in the range from 200 to 300 p. s. i. g. The compressed gas is passed through line 72 to cooler 74 which may be of the same type as cooler 66. A sponge oil may be added to line 72 through line 60. The effluent from cooler 74 passes through line 75 to separator or accumulator 76 from which a second liquid condensate fraction is removed through line 78. The liquid compressor condensate from lines 69 and 78 is combined in line 80 through which it passes to rectified absorber 52. The uncondensed gases pass from

5

accumulator 76 through line 81 to the rectified absorber. They represent the rich gas from which most of the components having three or more carbon atoms are absorbed into the absorption medium while components having one and two carbon atoms remain unabsorbed and leave the absorber as residue gas.

Rectified absorber 52 is operated in a manner well known to the art. It is, for example, equipped with trays such as bubble cap trays or turbogrid trays, indicated schematically on the drawing. Rich oil consisting of light gasoline components and lighter hydrocarbons is charged to the lower section of the absorber through line 80 and rich gas consisting of the unliquefied compressor effluent is charged through line 81. The rich oil and rich gas may be fed at the same plate in the absorber although it is preferable to feed the rich oil at a point some plates higher than the rich gas, as shown. The section of the column between the point at which rich gas is added and the point at which lean oil is added through line 51 is the absorption section. The lean oil passes down through the column while the vapor components pass upward in countercurrent contact therewith. In this process, the lean oil picks up the light hydrocarbon components having three or more carbon atoms per molecule which it is desired to recover. The unabsorbed vapors, consisting mainly of methane and ethane, pass upward beyond the point of injection of the lean oil into the uppermost section of the column which, as shown, is a sponge section. Sponge oil which consists of cooled heavy naphtha is added to the uppermost plate through line 46 and is removed from a drawoff tray through line 84. The sponge oil serves to recover a small portion of gasoline boiling range components, e.g., having five to six carbon atoms per molecule, which are carried out of the lean oil by the vapor stream passing up above the lean oil feed plate as well as some C_3 and C_4 hydrocarbons. The residue gas leaves the column through overhead line 85. The lean oil which has passed down through the column beyond the rich gas feed plate has at that point absorbed most of the light hydrocarbons having three or more carbon atoms per molecule which were present in the feed from lines 80 and 81 and may also have absorbed some undesired lighter hydrocarbons. The section below the rich oil and rich gas feed is a stripping section in which such lighter components are removed from the rich absorbing medium. The stripped oil passes as bottoms through line 86 to reboiler 89. The vaporized portion is returned to the column through line 88 to provide the necessary heat for the fractionation, and the liquid portion, which may be considered a rich absorber oil or an unstable catalytically cracked gasoline passes through line 90 to a further fractionation system which is conventional and is, therefore, not shown. The fractionation system generally consists of a debutanizer or stabilizer and a depropanizer. In the debutanizer, C_4 and lighter hydrocarbons are removed as overhead; the bottoms fraction is debutanized (stabilized) gasoline which is then used as a blending component for a gasoline motor fuel. The debutanizer overhead is split in the depropanizer into a C_3 and a C_4 cut.

A modification of the process of Fig. 1 is illustrated in Fig. 2. Fig. 2 shows the first and second condensers, 35 and 48, and associated accumulators, 36 and 49, and piping. Rectified absorber 200 is essentially identical in this system to rectified absorber 52 of Fig. 1 except that it is not provided with separate sponge oil and lean oil feed and with a separate sponge oil take-off plate. Instead, the intermediate condensate from accumulator 49 passes through line 201 containing cooler 202 to the uppermost plate of rectified absorber 200 from which it then passes downwardly in the same manner as the lean oil in absorber 52. Thus, the fraction serves both as sponge oil and as absorbing medium. In operating according to Fig. 2 it is desirable to adjust the partial condensation in condenser 48 in such a manner that the liquid in ac-

6

cumulator 49 contains only a very low concentration of components having five to six carbon atoms per molecule; the liquid consists mainly of gasoline components of seven to ten carbon atoms per molecule. In the operation according to Fig. 2, the first condensate from line 38 is withdrawn from the system as illustrated in Fig. 1 by line 45.

Fig. 3 illustrates a useful but less-preferred method of operating the process of this invention. Except for the piping arrangements, the apparatus in Fig. 3 is essentially identical in all respects to the apparatus in Fig. 1. The same numbers have been used throughout, wherever possible, and the description will not be repeated.

An important processing difference between the process of Fig. 3 and that of Fig. 1 is that fractionator 15 is operated in such manner that the vapor overhead in line 16 excludes the heavy naphtha component. Thus, the vapor overhead in line 16 consists essentially only of gasoline and lighter-boiling hydrocarbons. In such an operation the heavy naphtha must be removed from the fractionator. This may be done either by including it in the light gas oil fraction taken from line 21 or by removing a portion of the internal reflux from line 31 through line 301. As a consequence of having no heavy naphtha in the overhead from the fractionator, the first partial condensate which is gathered in accumulator 36 is essentially a heavy gasoline fraction, while the condensate in accumulator 49 is an intermediate gasoline fraction and that in accumulator 55 a light gasoline fraction. The condensate from accumulator 36 is excellently suited to be used as lean oil in rectified absorber 52. It is passed to the absorber through line 302 containing cooler 303. The intermediate and light partial condensates are removed from accumulators 49 and 55 through lines 304 and 305, respectively. These fractions may be disposed of in either of two ways, essentially similar to the disposal of the light condensate from accumulator 55 in Fig. 1. Thus, the intermediate and light condensate may be passed to header 306 and from there through line 308 to line 80, the rich oil feed line to the absorber. Alternatively, the intermediate and light condensates may pass through lines 309 and 310 to lines 311 and 312 to be used as sponge oil for the compressors. The intermediate condensate may also be used as a premium gasoline blending compound without further processing.

In the operation illustrated in Fig. 3, a suitable sponge oil from an extraneous source, which may be, for example, a cooled portion of the light gas oil from line 21, is passed to absorber 52 through line 314 and withdrawn from the drawoff plate above the lean oil feed plate through line 315. In an alternative operation, not illustrated, the first partial condensate from accumulator 36 passes directly to the topmost plate of the absorber to serve as sponge oil and absorber oil.

An alternative method of carrying out the partial condensation of the fractionator overhead is illustrated by Fig. 4. The vapor overhead from column 15 passes through line 16, in which it is contacted with a relatively cool liquid fraction, from a source described hereafter, which is added to it through line 408. The liquid fraction provides sufficient cooling to condense the heaviest components of the vapor stream in line 16 while light components in the fraction from line 408 are evaporated. The liquid vapor mixture passes to separator 401, which may be an accumulator or knockout drum or cyclone, in which a heavy liquid fraction essentially like that gathered in accumulator 36 of Fig. 1 is removed through line 409 to be disposed of as in Fig. 1 or Fig. 2. The overhead from separator 401 passes to a partial condenser 402 which is similar to any of condensers 35, 48 or 54 of Fig. 1. The condenser effluent passes to accumulator 404 in which a liquid fraction essentially like that gathered in accumulator 49 of Fig. 1 is recovered. This fraction is taken through line 406 to be disposed of in part in the same manner as the liquid from accumulator 49 in Fig. 1.

The remainder of this fraction passes through line 408 to be admixed with the vapor effluent from the fractionator to provide the required cooling. The vapor taken from accumulator 404 through line 405 may pass to a further partial condenser or to the compressors.

In the process of Fig. 1 the fractionator overhead temperature in line 16 is about 240°–280° F. The effluent temperatures from condensers 35, 48 and 54 are 180°–220° F., 140°–160° F. and 90°–110° F., respectively. Lean oil enters the absorber at about 60°–100° F. and sponge oil at about 90°–100° F. The remaining temperatures in the catalytic cracking unit, fractionating unit and compressor and absorber systems are conventional.

In the process of Fig. 3 the fractionator overhead temperature in line 16 is about 200°–225° F. and the effluent temperatures from condensers 35, 48 and 54 are in the ranges of 160°–190° F., 125°–150° F. and 90°–110° F., respectively.

In the process as illustrated by Figs. 1 and 3, the use of three partial condensers and associated accumulators is shown. The process may also be operated with a plurality of partial condensers other than three, e.g., two or four. Other modifications of the process of this invention will occur to those skilled in the art.

I claim as my invention:

1. A process for recovering catalytically-cracked gasoline having a relatively low end point which comprises fractionally distilling the product from conventional catalytic cracking of hydrocarbons, taking overhead a vapor fraction comprising gasoline boiling range and lighter hydrocarbons, partially condensing said overhead fraction to produce at least one liquid partial condensate fraction comprising gasoline and substantially excluding hydrocarbons in the boiling range of heavy catalytically-cracked naphtha, partially condensing the remaining vapor fraction to produce at least a second, lighter liquid partial condensate fraction and an uncondensed gas fraction, compressing said uncondensed gas fraction and cooling the compressed gas to produce at least one liquid compressor condensate fraction and a compressed gas fraction, charging said liquid compressor condensate fraction and said compressed gas fraction to the lower section of a rectified absorber, charging at least part of said first-mentioned partial condensate fraction to the upper section of said absorber as lean oil, causing gas to flow upwardly in said absorber in countercurrent contact with said lean oil and withdrawing from said absorber as overhead a lean residue gas and as bottoms unstable catalytically-cracked gasoline.

2. A process in accordance with claim 1 in which said second-mentioned partial condensate fraction is included in the charge to the lower section of said rectified absorber.

3. A process in accordance with claim 1 in which said second-mentioned partial condensate fraction is added as

compressor sponge oil to the vapors flowing from the compressor to the compressor cooler.

4. A process in accordance with claim 1 in which said first-mentioned partial condensate fraction is charged to the topmost plate of said rectified absorber and no side stream is removed from said absorber.

5. A process in accordance with claim 1 in which a sponge oil is charged to the topmost plate of said rectified absorber and the total liquid flowing in the upper section of the absorber is removed from a take-off plate at a point above that at which the lean oil is introduced.

6. A process for recovering catalytically-cracked gasoline having a relatively low end point which comprises fractionally distilling the product from conventional catalytic cracking of hydrocarbons, taking overhead a vapor fraction consisting of heavy catalytically-cracked naphtha and lighter hydrocarbons, partially condensing said overhead fraction to produce at least one liquid partial condensate comprising said heavy catalytically-cracked naphtha, partially condensing the remaining vapor fraction to produce a liquid partial condensate comprising gasoline and substantially excluding hydrocarbons in the boiling range of heavy catalytically-cracked naphtha, partially condensing the remaining vapor fraction to produce another lighter liquid partial condensate fraction and an uncondensed gas fraction, compressing said uncondensed gas fraction and cooling the compressed gas to produce at least one liquid compressor condensate fraction and a compressed gas fraction, charging said liquid compressor condensate and said compressed gas fraction to the lower section of a rectified absorber, charging said second-mentioned partial condensate fraction to the upper section of said absorber as lean oil, causing gas to flow upwardly in said absorber in countercurrent contact with said lean oil, and withdrawing from said rectified absorber as overhead a lean residue gas and as bottoms fraction an unstable catalytically-cracked gasoline.

7. A process in accordance with claim 6 in which said first-mentioned partial condensate is charged to the topmost plate of said rectified absorber as sponge oil and all liquid flowing downwardly in the topmost section is withdrawn from the column as a side stream from a take-off plate above the point of addition of said lean oil.

8. A process in accordance with claim 6 in which said first-mentioned partial condensate is stripped of gasoline and lighter components and the bottoms fraction consisting of heavy catalytically-cracked naphtha is withdrawn from the system.

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