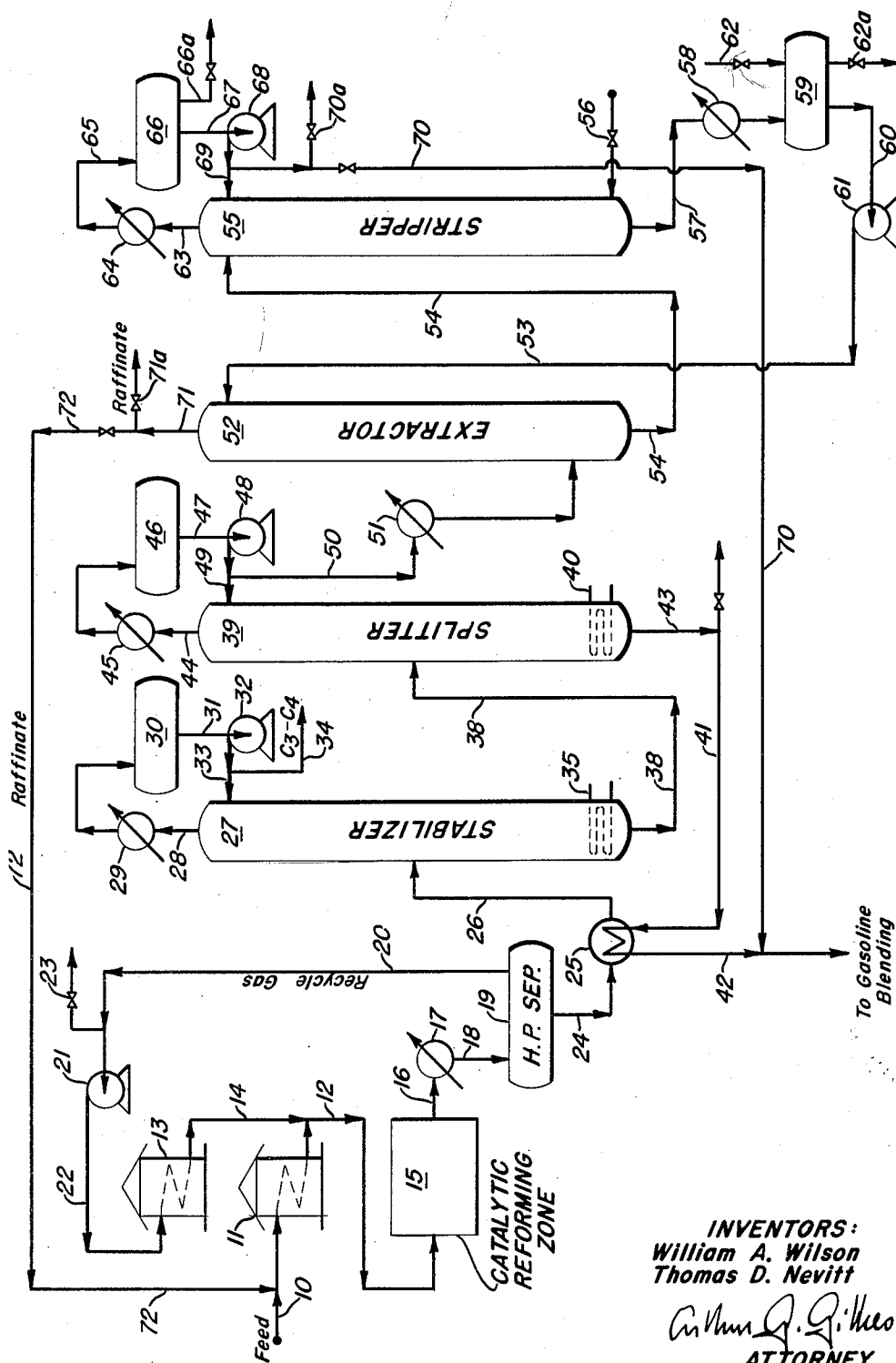


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COMBINATION REFORMING AND SOLVENT EXTRACTION PROCESS

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COMBINATION REFORMING AND SOLVENT EXTRACTION PROCESS

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4 Claims. (Cl. 208—96)

This invention relates to improvements in the production of high octane number blending stock, i.e. 98 CFR-R clear or higher, from relatively low octane naphthas by catalytic reforming. In one aspect, the invention is concerned with providing a process integrating the reforming operation with fractionation and extraction and using a particular solvent of high capacity for aromatics so as to provide economies in the reforming process and remove processing limitations characteristic of reforming processes of present design. In another aspect, the invention provides a process for producing high yields of 98+ CFR-R clear gasoline blending stock while conducting the reforming operation at a severity producing reformate of lower octane so as to significantly reduce operating costs and catalyst requirements.

Steadily increasing octane levels for both premium and regular gasoline have created serious refining problems. The problems are basically economic in nature because within the limits of high quality feed stock and catalyst availability, it is possible, theoretically at least, to produce gasoline of the present octane level and that project for the near future. The increasing volume of the demand for high octane premium gasoline (i.e. about 98 CFR-R and higher) however is working a serious dislocation in the structure of the domestic refining industry. In general, refiners have been relying on the existing large capacity of catalytic cracking facilities to produce high octane base stocks for premium gasoline production. Reforming has been used in general to upgrade virgin and other low-grade naphthas to permit blending into the total gasoline pool (premium plus regular) without disturbing the weighted average octane number of the pool necessary to meet competition. In some instances where high quality naphthas containing relatively high percentages of naphthenes were available, reforming has also been used to produce special, high octane blending stock. However, as octane requirements for premium have reached the 98+ CFR-R level, the limit of feasibility of catalytic gasoline as the major premium base stock is reached because catalytic gasoline rarely exceeds about 92-93 CFR-R clear and is not high enough in blending octane to blend up to above the 97 level in leaded gasoline. Thus, a drastic shift in the function of catalytic reforming is demanded, but as the level of reforming severity is lifted to meet premium blending standards instead of regular or pool blending standards, reforming costs are greatly magnified. There is a pronounced drop-off in recoverable liquid yield of reformate as reforming severity is increased. Hence, there is an effective decrease in reforming plant capacity. Reforming catalyst life also is sharply reduced as severity is increased. The operating costs per barrel are increased, and since catalyst cost is a major cost factor, the effect is a significantly increasing factor in the incremental cost of the higher octane gasoline. Space velocity (the rate of flow of feed in units of feed flow per unit of catalyst charge) must be reduced to achieve higher octane levels with the same catalyst so

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that again plant capacity is lost, or catalyst inventory must be significantly increased. Because of an apparent shift in the relative extent to which the various reforming reactions occur at the higher severities, particularly above 95 octane, more frequent catalyst regeneration becomes necessary so that costs rise and, with feeds that are lean in naphthenes, may make production of 98+ stock by such means totally non-competitive. Hence, the availability of suitable feed stocks by economical upgrading, the character of the feed and its availability become determinative factors in the cost and volume of premium gasoline production.

This summary of the economic situation affecting reforming indicates that conventional once-through catalytic reforming suffers severe potential limitations in meeting rising octane goals. As an alternative to once-through, regenerative reforming, several schemes involving extraction of reformates followed by recycle or separate reforming of the raffinate have been proposed. In a sense, these processes substitute selective extraction of reformate and raffinate rerunning for reforming severity and catalyst regeneration. They attempt to operate for relatively long periods without regeneration by using high pressures of hydrogen, e.g. 500-750 p.s.i.g. They are costly both investment-wise and in operation, and they encounter limitation in the potential barrel-octanes of high octane gasoline producible because, for example, of unfavorable equilibrium conditions encountered in the reforming step. Nevertheless, they have commanded attention because they have seemed the most logical, and perhaps only reasonable alternatives, to increasing once-through severity by catalyst and process design means.

The present invention applies a number of new operating factors. It has been found that there is a relationship between reforming severity, particularly with the use of a platinum type reforming catalyst in a low pressure operation, and the distribution of aromatics in the reformate. As the reforming severity reaches the level of about 90 CFR-R octane clear, and particularly as it exceeds 95 octane clear, the concentration of aromatics in the heavier portion of the reformate becomes such that upwards of 40 to 65 volume percent of a heavy fraction containing at least about 75 volume percent aromatics can be recovered by simple fractionation at a cut-point in the range of about 220° to 300° F. Such stocks have extrapolated octanes exceeding 100 CFR-R clear. At severity levels below 90 octane clear, there is considerable variation in the relationship of octane number vs. aromatics content with the source of the naphtha feed, that is whether the feed is a high naphthenic Mid-Continent naphtha or a paraffinic type Middle East naphtha, for example. Surprisingly, above 90 octane number it has been found that the nature of the feed source is immaterial so that a high octane heavy reformate can be produced from any feed of appropriate boiling range by correlation of reforming severity with reformate cut-point based on aromatics content. The light reformate, usually comprising about 35 to 60 volume percent of the total, is of relatively low octane number, e.g. about 75 to 80 CFR-R clear, but at these reforming severities will contain a considerable amount of aromatics which can be selectively extracted at relatively low cost to provide aromatics rich extracts of high octane for blending with the heavy reformate while eliminating low octane components as raffinate for recycling to the reforming operation or for other use.

Solvent extraction however, is inherently an expensive process, both investment-wise and in operation. According to the present invention, therefore, the cost of extraction is minimized by treating only that portion of the reformate which will produce a substantial benefit

in barrel-octanes and by using a solvent having properties particularly adapted to the process. Thus, it has been found that even a highly efficient extraction performed on heavy reformate produced by splitting a 90+ reformate at a cut point in the range of about 220 to 300° F. increases the octane only about 1 to 2 units. On the other hand, a light fraction resulting from the splitting operation, typically having an octane of about 70 to 80 CFR-R, can be treated by extraction to recover about 35 to about 65% of 98+ octane material. The size of the components of the extraction unit including the extraction and stripping towers, the solvent inventory and the solvent handling facilities may be reduced by as much as one third. Moreover, conventional solvents of sufficient selectivity to separate 98+ octane material from low octane reformates in general have rather low capacity for aromatics. Hence, large solvent inventories with over-sized extraction and stripping towers are required. It has been found that gamma-butyrolactone has unusual capacity for aromatics together with the selectivity for effecting the desired separation of high octane blending stock from light reformate. For example, at 77° F. and in the absence of water, butyrolactone extracts about four times the volume of aromatics as an equal volume of diethyleneglycol.

According to the present invention, the naphtha charge stock is reformed in the presence of a reforming catalyst, advantageously a platinum containing reforming catalyst, and hydrogen recycle gas at a severity producing a reformate of at least about 90 CFR-R clear. The resulting reformate is fractionated to separate a heavy reformate fraction containing at least about 75 volume percent aromatics and a light reformate fraction having an end point in the range of about 220° to 300° F. The light reformate fraction is contacted with a selective solvent comprising butyrolactone to extract an aromatics rich extract of high octane number, advantageously 98 CFR-R clear or higher. The extract is separated from the solvent and may be blended with the heavy reformate fraction in the production of high octane gasoline. The raffinate advantageously is recycled to the reforming step, although it can be blended with other refinery streams, or can be upgraded in a separate conversion process such as isomerization or dehydrocyclization. It is advantageous to separate C₅ and lighter hydrocarbons from the light reformate fraction before the solvent extraction. A particular advantage of the process is that the extract can be separated from the butyrolactone solvent simply by steam stripping. Butyrolactone has a relatively low boiling point of 403° F. approximating the usual gasoline end point but by contacting only light reformate fractions boiling below 300° F. as in the invention, the solvent and extract can be readily separated by distilling under stripping conditions. There is no need to resort to washing with water or other solvents with the attendant problems of recovering the solvent and/or the wash medium for reuse.

In conducting the reforming operation, it is advantageous to use relatively low hydrogen pressure, e.g. in the range of about 50 to 400 p.s.i.g., so as to promote dehydrocyclization of paraffins in the charge. It is also specially advantageous to restrict severity to that producing about a 93 to 98 CFR-R reformate. Yield in barrel-octanes is increased thereby; maintenance of catalyst activity is improved, reducing the required frequency of regeneration; and catalyst life is conserved. For an existing plant, flexibility with respect to feed, catalyst and design limits is provided.

In the drawing, the naphtha feed through line 10 is charged to a conventionally fired heater 11. The preheated feed in line 12 may be combined with hot recycle hydrogen gas from heater 13 and line 14. The charge mixture is contacted in reforming zone 15 with a reforming type catalyst in a manner and under reforming conditions described in further detail below. The reformed

mixture passes via connection 16 to cooler 17 and thence via connection 18 to high pressure separator 19. Gas, predominantly hydrogen, is separated from vessel 19 through line 20 for recycle by means of a recycle compressor or blower system 21 and line 22. The net production of gas in the process may be withdrawn from the system as by connection 23. The liquid reformate separated in vessel 19 is withdrawn through line 24 and is charged via preheater 25 and line 26 to debutanizer or stabilizer tower 27. In typical operation, light ends are taken overhead from tower 27 through line 28 and cooler 29 to receiver 30. A portion of the liquid collected in receiver 30 is returned to tower 27 as reflux through line 31, pump 32 and connection 33. The remainder, usually comprising a mixed C₃-C₄ light hydrocarbon fraction is withdrawn through line 34. An internal reboiler tube 35 is shown as an additional source of heat.

The stabilized reformate is withdrawn from tower 27 by line 38 and is charged to splitter tower 39. Heat is supplied as shown by internal reboiler tube 40. The operation of splitting tower 39 is controlled to remove the heavy reformate fraction containing upwards of about 75 to 80 volume percent aromatics (100+ octane) through line 43. A lighter fraction is taken overhead through line 44 and cooler 45 to receiver 46. A portion of the liquid collected in receiver 46 is returned to the tower top by means of line 47, pump 48 and line 49. The heavy reformate in line 43 may be used, as a source of preheat via exchanger 25, as shown, before pumping to gasoline blending facilities through lines 41 and 42.

The net product is a low octane light reformate having an end point in the range of about 220 to 300° F. which is charged by means of line 50 and heat exchanger 51 to solvent extractor 52. In extraction tower 52, the light reformate is countercurrently contacted with solvent admitted to the top of the tower through line 53. A stream comprising solvent plus extract is withdrawn from the bottom of tower 52 through line 54 and is charged to solvent stripping tower 55. The extract is stripped from the solvent in stripping tower 55 at reduced pressure, advantageously with the aid of steam admitted at the bottom of the tower through line 56. The stripped solvent is withdrawn from the bottom of tower 52 through line 57 and cooler 58, and is collected in solvent accumulator 59 from which it is recirculated to extractor tower 52 by means of line 60, pump 61 and line 53. Make-up solvent can be added as indicated by connection 62, and a portion of the solvent inventory can be withdrawn through 62a for treatment, as by water washing and/or distillation, to prevent build-up in impurities. The extract is recovered from the top of tower 55 through line 63, cooler 64 and line 65, and is collected in extract receiver 66. Water condensate is removed from the bottom of the receiving drum as by line 66a. Reflux can be returned to the top of stripper 55 from receiver 66 via line 67, pump 68 and connection 69. The net production of aromatic extract can be directly blended via line 70 with the heavy reformate in line 41 for transfer to gasoline blending facilities, or can be subsequently so blended. The raffinate from the extraction is recovered as overhead from tower 52 through line 71 and can be recycled to the reforming step via line 72.

As indicated above, it is essential that the reforming process conducted in zone 15 be conducted under conditions of severity resulting in a C₅+ reformate of at least about 90 octane number clear. Also, to obtain the desired distribution of aromatics in the reformate, the reforming should be conducted at relatively low pressure favoring dehydrocyclization rather than hydrocracking. Ordinarily, the average reaction temperature should be in the range of about 850° F. to 1000° F. at a pressure in the range of about 50 to 400 p.s.i.g., advantageously about 200 to 300 p.s.i.g. The recycle hydrogen rate should approximate 1,000 to 10,000 cubic feet per barrel. The space velocity will depend on the activity

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of the catalyst but ordinarily will be in the range of about 0.1 to 5.0 WHSV. Advantageously, the catalyst is of the platinum-alumina type containing about 0.1 to 1.0 weight percent platinum. The catalyst can be employed in the form of a fixed bed of pelleted, beaded or extruded particles, or may be employed in the form of a moving bed, or in fluidized form as a finely divided powder. In fixed bed processes, a series of two or more, usually 3 to 5 reactors are used with interheaters between the reactors so that temperature drop due to the endothermic nature of the major reactions can be compensated for. Operating at the desired severity levels and at low pressure requires more or less frequent regeneration of the catalyst. This can be provided by a controlled process for burning off carbon deposits, advantageously followed by an elevated temperature "soak" with oxygen enriched gas. Advantageously, a "swing" reactor as used in the Ultraforming process is provided so that cyclic regeneration can be affected without shutting down the unit.

The fractionation incident to the invention can be conducted with considerable flexibility. For example, it may comprise separation of recycle gas after cooling at approximately reaction pressure followed by stabilization of the condensed reformat, as shown in the drawings, or it may comprise partial condensation of the heavier components of the reformed mixture followed by separation of recycle gas, stabilization and such further fractionation of the lighter components as is desired. In any event, the essential fractionation is splitting the reformat into a heavy reformat fraction containing at least about 75 to 80 volume percent aromatics and a lighter reformat fraction. The lighter fraction may comprise the overhead from the initial boiling point of the C_5+ reformat to an end point in the range of 220 to 300° F. depending upon the reforming severity. Alternatively, the lighter components, including C_5 's and C_6 's, may be separated so that the light reformat essentially comprises a C_6+ , C_7 or C_7+ fraction. The light reformat is charged to a selective extraction producing an aromatics rich extract suitable in octane for blending with the heavy reformat and a raffinate of low octane. If a C_5 fraction rich in isopentane has been segregated from the lighter reformat by prefractionation it may have a blending octane high enough to permit reblending with the high octane heavy reformat. If the low octane raffinate is to be recycled to the reforming zone, or is to be separately reformed, it is usually desirable to separate S_6- hydrocarbons by prefractionation since the lighter hydrocarbons are difficult to convert under reforming conditions.

The initial boiling point of the heavy reformat fraction is correlated according to the invention, as noted above, with the reforming severity. For example, charging a C_7+ heavy naphtha of 212° to 404° F. boiling range and 46.7 CFR-R octane (52% naphthenes), the octane of 220° to 430° F. heavy reformat was 96.4 CFR-R at 72 volume percent yield based on the C_5+ reformat or 60.8 volume percent based on the naphtha feed. With a reformat severity of 99.5 CFR-R the 220° to 430° F. fraction had an octane number of 102.9 CFR-R clear with 70.2 and 54.5 volume percent yields on reformat and feed, respectively. Concomitantly, there was an increase in the octane of the 270° to 430° F. heavy reformat from 98.8 to 104.8. A particular factor appears to have been the large relative gain in quality of the 220° to 270° F. fraction as severity was increased. The octane gain of this fraction was from 77 CFR-R clear for a 93 octane reformat to 97 for a 100 octane reformat. Accordingly, it is preferable to include this material in the heavy reformat when the reforming severity is above 95 octane, but at lower severities, it is better to split at a higher cut-point nearer the 270° to 300° F. range.

It is an essential feature of the present invention that only the light reformat fraction is extracted for re-

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covery of premium gasoline blending stock and separation of low grade raffinate for reprocessing. In this way, the cost burdens of the inherently expensive separation necessary to segregate hydrocarbons by type are greatly reduced. The size of the extraction equipment can be minimized, thus reducing investment cost and the expense of solvent inventory. Operating costs are greatly reduced because it is so much cheaper to strip the lower volume of light hydrocarbons from the solvent.

Butyrolactone has a specific gravity of 1.124, a boiling point of 403° F., and a freezing point of -47° F. It is immiscible with hexane and miscible with benzene and water. Thus, its gravity is sufficiently greater than that of the naphtha to be extracted to facilitate counter-current flow and phase separation in an extraction column. One or more columns, or extraction stages can be used, but ordinarily a single tower of about 5 to 10 stages will be found suitable. The extraction can be conducted at any temperature from the freezing point to below the boiling point, but selectivity of the solvent is appreciably better in the lower temperature ranges. A temperature in the range of about 60 to 100° F. is preferred. Selectivity can be increased somewhat by the addition of water or other diluents or antisolvents. Since the extraction is advantageously conducted at a temperature below the boiling range of the reformat feed, atmospheric pressure can be employed.

In operation, the aromatics are extracted by the solvent, and the extract is separated from the rich solvent in a separate zone, advantageously a simple stripping column using steam as the stripping agent. The extract, and also the raffinate, can be water washed if desired to remove tracts of solvent. Solvent then can be recovered from the wash water by distillation for recirculation to the extraction system. Accumulated impurities can be removed from the solvent as necessary by flashing solvent overhead in a solvent regenerator tower. Because of the higher capacity of butyrolactone solvent for extracting aromatics relative to better known solvents such as glycols, the solvent flow to the extractor is considerably reduced. The result is substantial savings in the way of smaller equipment such as the extractor tower, stripper tower, and solvent accumulator drum. Less steam is required to strip the smaller amount of solvent. Thus, the stripper reboiler, the overhead condenser and the extract receiver may be smaller.

In a specific example of operation according to the invention, 15,000 barrels per day of Mid-Continent naphtha are reformed in the presence of a catalyst comprising 0.6% platinum-on-alumina. The reforming conditions include an average temperature of 900° F. at a pressure of 300 p.s.i.g., with a space velocity of 1-2 WHSV and a recycle rate of 5000 s.c.f./barrel of feed. The effluent from the reforming operation is cooled to 120° F. in order to separate recycle gas in a high pressure separator at a pressure of about 250 p.s.i.g. The 12,400 b./d. of liquid product recovered is stabilized in a debutanizer tower operated at 185° F. at the tower top and 470° F. at 205 p.s.i.g. at the tower bottom. 1270 b./d. of C_3 and C_4 hydrocarbons are taken overhead. The stabilized reformat (95 CFR-R octane) is charged at the rate of 11,130 b./d. to a stripper tower operated at 440° F. tower top temperature maintaining a pressure of 160 p.s.i.g. at the tower bottom. The heavy reformat having an initial boiling point of 270° F. is recovered at the rate of 7630 b./d. and has an octane of 102 CFR-R clear. The light reformat recovered overhead at the rate of 3500 b./d. has an octane of 77 CFR-R clear.

The light reformat is cooled to 100° F. and is charged to an extractor tower operated at 100° F. and 15 p.s.i.g. 3750 b./d. of butyrolactone solvent are charged to the top of extractor tower, which is designed to provide six theoretical stages at a solvent to oil ratio of 1.13. A 60 CFR-R raffinate is separated at the rate of 2210 b./d. and may contain up to about 20 b./d. of butyrolactone

recoverable by water washing. The rich solvent from the base of the extractor is charged to a solvent stripper operated at 250° F. at the top and at 300° F. and 5 p.s.i.g. at the base where about 15,000 pounds per hour of steam are introduced as stripping aid. The extract (98 CFR-R) is recovered overhead at the rate of 1305 b./d. Solvent is withdrawn from the bottom of the stripper tower through a cooler to an accumulator from which it is recirculated to the extractor.

The advantages of operation according to the invention may be perceived by comparing the barrel-octanes of gasoline recovered at a severity of 93.5 for the C₅+ reformate, which is then treated by successive fractionation and extraction with butyrolactone to recover 100 octane+blending stock, with the barrel-octanes recovered by once-through reforming to 100 octane severity. The total barrel-octanes recovered from the latter operation is 7,700 while the total recovered according to the invention is 8,895, of which 68 volume percent is 101 CFR-R clear octane value, with the balance raffinate suitable for recycle or blending into regular gasoline.

In the production of high octane gasoline blending stock, there is a strong incentive for going to severities above the 95 octane level because of the marked concentration of aromatics in the heavier fractions of the reformate and the increasing potential yield of 100+ octane stock by fractionation plus extraction. On the other hand, the penalties for operating at high severities rapidly become greater as the octane level of once-through reforming approaches 100. There is a pronounced increase in drop-off in yield above about the 95 level, and there is an increasing amount of light hydrocarbons in the C₅- range produced. The catalyst requires more frequent regeneration, and with stocks which are lean in naphthas or with which cracked stocks contain substantial quantities of olefins, the amount of coke formation is increased to an extent requiring excessively frequent regeneration. Operating costs are increased thereby, and capacity is reduced. In addition, a substantially higher inventory of catalyst is required, and the effective life of the catalyst is significantly reduced.

Contrary to the prevailing opinion that the heavy paraffins in heavy reformate are of such low octane value that their removal necessarily results in appreciable octane improvement, it has been found in the development of the invention that only small increases in the octane of heavy fractions containing upwards of 80% aromatics are obtained by further extraction. Thus, extraction of a 270° F.+ heavy reformate having an octane of 102 CFR-R with silica gel improved the octane only from 100+0.2 cc. TEL to 100+0.36 at a percentage sacrifice in yield from 47.1 to 40.3, based on the total reformate.

We claim:

1. A process for producing high octane gasoline blending stock from low octane naphtha charge stock by catalytically reforming at less than once through reforming

severity which process comprises reforming a naphtha charge stock consisting of a C₇+ naphtha boiling in the range of about 200 to 400° F. in the presence of a platinum-alumina type reforming catalyst, said catalyst containing from about 0.1 to 1.0 weight percent platinum, and recycle hydrogen, under a combination of conditions including a temperature in the range of about 850° F. to 1000° F., a pressure in the range of about 50 p.s.i.g. to 400 p.s.i.g., a weight hourly space velocity in the range of about 0.1 to 5.0 and a hydrogen recycle rate in the range of 1000 to 10,000 cubic feet per barrel, thereby providing a severity so as to produce a total C₅+ reformate having an octane number of at least about 95 CFR-R clear; fractionating said reformate at a cut point in the range of about 220° F. to 270° F. to obtain a light fraction boiling in the range of C₅+ to said cut point comprising about 35 to 60 volume percent of the total C₅+ reformate and a heavy fraction boiling in the range of said cut point to about 430° F. comprising about 40 to 65 volume percent of the total C₅+ reformate and containing at least 75 volume percent aromatics; wherein said cut point is at about 270° F. when said total C₅+ reformate octane number is about 95 CFR-R clear and said cut point is decreased towards 220° F. as the octane number of said total C₅+ reformate increases above 95 CFR-R clear; contacting said light fraction with a selective solvent comprising butyrolactone to separate an aromatics-rich extract of high octane number and a low octane raffinate; separating said aromatics-rich extract from solvent; recycling solvent to said solvent extraction zone; and thereafter blending said aromatics-rich extract with said heavy fraction to obtain a high octane gasoline blending stock.

2. The process of claim 1 in which C₅ and lighter hydrocarbons are separated from said light fraction prior to said extraction.

3. The process of claim 1 in which said low octane raffinate is recycled to the reforming step.

4. The process of claim 1 in which said aromatics-rich extract is separated from solvent by steam stripping.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 2,956,006

October 11, 1960

William A. Wilson et al.

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 1, line 36, for "project" read -- projected --;
column 5, line 48, for "S" read -- C₆ --.

Signed and sealed this 25th day of April 1961.

(SEAL)

Attest:

ERNEST W. SWIDER

Attesting Officer

DAVID L. LADD
Commissioner of Patents