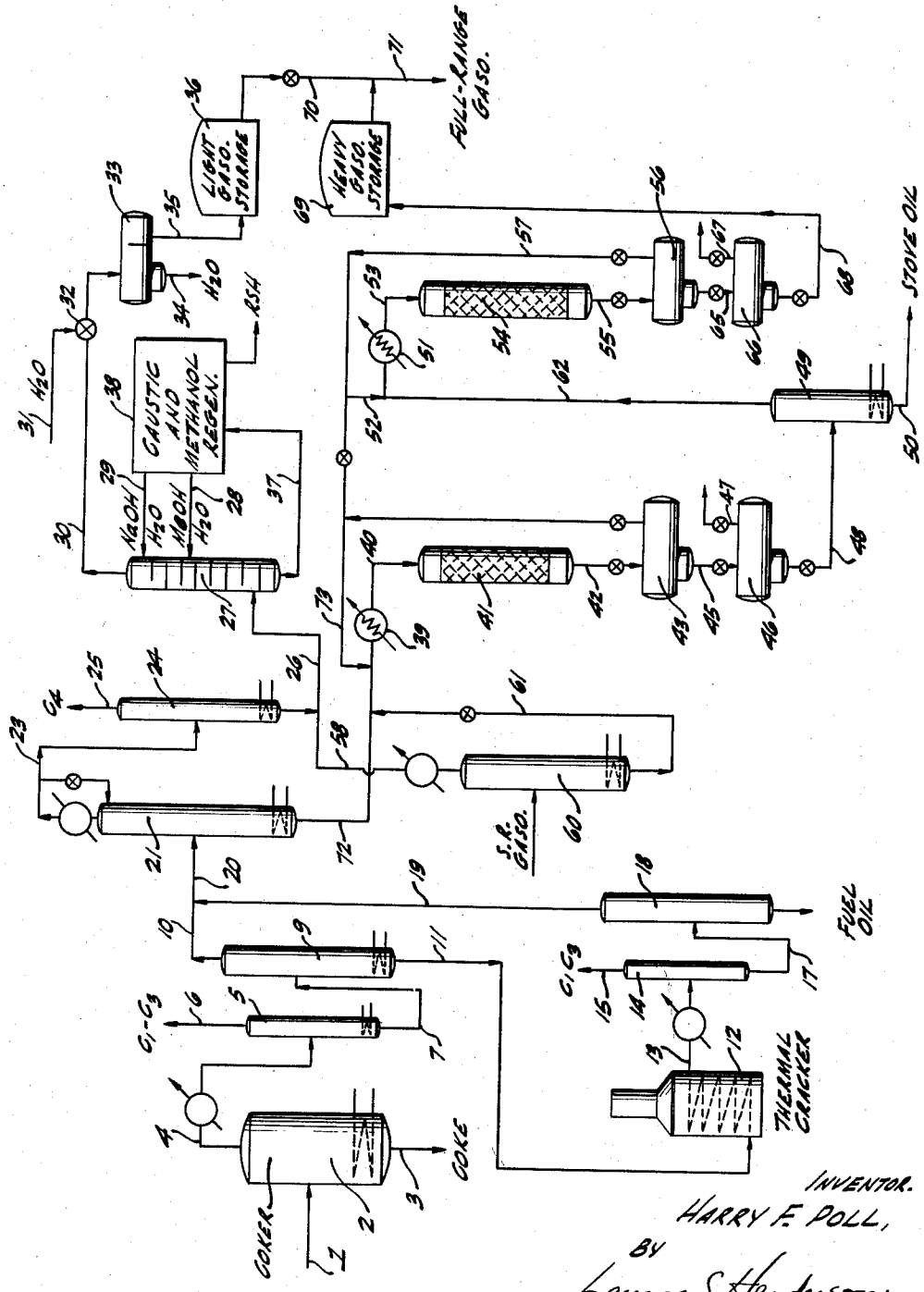
Oct. 13, 1959

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2,908,626

PROCESS FOR CATALYTIC DESULFURIZATION AND REFORMING OF CRACKED NAPHTHAS

Filed March 26, 1956



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United States Patent Office 2,908,626
Patented Oct. 13, 1959

2,908,626

PROCESS FOR CATALYTIC DESULFURIZATION AND REFORMING OF CRACKED NAPHTHAS

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Application March 26, 1956, Serial No. 573,837

9 Claims. (Cl. 208—54)

This invention relates to a combined process for desulfurizing and reforming thermally cracked, high-sulfur naphthas to obtain maximum yields of high-octane, low-sulfur naphthas. Briefly, the process includes the following steps:

(1) Fractionating a full-range, thermally cracked naphtha to obtain a light C_5–C_6 fraction substantially free of thiophene sulfur, and having an ASTM maximum boiling point between about 170° and 200° F.;

(2) Subjecting the light fraction to caustic washing or other suitable treatment for the removal of mercaptan sulfur;

(3) Treating the heavy naphtha fraction from step 1 with hydrogen in a catalytic hydrodesulfurization zone containing a cobalt molybdate catalyst to effect substantially complete desulfurization;

(4) Treating the desulfurized product from step 3 in a catalytic reforming zone in the presence of hydrogen to effect a substantial improvement in octane rating thereof; and

(5) Blending portions of the caustic-treated, low boiling fraction from step 2 with a portion of the reformed product from step 4.

It has been found that by splitting the feedstock as outlined in step 1, and treating the two fractions separately as described, the reblended product, is (1) higher in octane rating than if the total feedstock were treated under like conditions by catalytic hydrodesulfurization and reforming, and (2) lower in sulfur and higher in octane rating than if the entire stock were treated by the caustic washing of step 2, followed by reforming. These advantageous results stem in part from the specific nature of the feedstock which is treated in the fractionation step 1. It is known that the gasoline fractions produced by thermal cracking of high-sulfur, naphthenic crudes contain both mercaptan sulfur and the more refractory types containing thiophene rings. It has been found that a large portion of the mercaptan sulfur occurs in the low boiling fraction of these naphthas, and that upon fractional distillation the thiophene type compounds, which are not removable by caustic treating, are almost wholly retained in the high-boiling fraction, even though thiophene, and thiophene azeotropes of hydrocarbons present in the feed, may individually boil substantially within the distillation temperature range of the overhead fraction.

The principal object of the invention is to effect an overall desulfurizing and reforming of thermally cracked, high-sulfur gasolines to obtain maximum yields of high-octane gasoline, or conversely maximum octane rating at a given liquid yield. A specific object is to avoid the treatment in the desulfurizer and the reformer of the low-boiling portions of the feedstock, inasmuch as these portions are not improved, and may be degraded, by catalytic reforming. Another object is to utilize to the most economical advantage the treating capacity of any given reforming and desulfurizing installation by avoiding the treatment therein of materials not benefited. A still further object is to avoid the hydrogenation of high anti-

knock olefins present in the low boiling portions of the feedstock. A still further object is to minimize, in a catalytic reforming-catalytic desulfurization combination, the hydrogen consumption in the desulfurizer, thereby minimizing the portion of straight run gasoline which must be treated in the reformer in order to produce sufficient hydrogen to supply the desulfurizer. A specific object is to provide means for fractionating high-sulfur, thermally cracked naphthas whereby an overhead fraction containing the bulk of the C_5 and C_6 hydrocarbons may be obtained, while excluding therefrom any substantial amounts of compounds containing thiophene rings. Other objects and advantages will be apparent from the more detailed description which follows.

It is well known in the art that most catalytic reforming processes do not benefit all portions of the feedstock to the same degree. Specifically, it is known that materials such as cyclohexane, methyl cyclopentane, and olefins boiling in the same range are better excluded from the reformer feed. The benzene produced by dehydrogenation of cyclohexane and the isomerization and dehydrogenation of methyl cyclopentane has a lower anti-knock value than the original cyclohexane or methyl cyclopentane. The olefins will be largely converted to paraffins having a lower anti-knock value than the original olefins. For all these reasons it has sometimes been considered desirable to remove such low-boiling materials from the reformer feed.

However, the picture is changed when one considers a naphtha feedstock derived by thermal cracking of high sulfur crude oils, and which must be desulfurized prior to reforming. Such naphthas may contain from about 0.5% to 6% by weight of total sulfur, and such sulfur is normally distributed as both mercaptans and cyclic compound such as thiophene. The thiophene-ring compounds are particularly prevalent in thermally cracked naphthas, including coker distillates. Thiophene boils at 183° F., while cyclohexane boils at 177° F. Other hydrocarbons are present which boil very close to these materials. It would hence appear extremely doubtful whether any significant portion of the C_5–C_6 hydrocarbons could be recovered by simple distillation without carrying along considerable amounts of thiophene and methyl thiophenes. The methyl thiophenes boil at about 234°–240° F., and the presence of their azeotropes in the 110–180° fraction might be expected. It has been found however that the thiophene/methyl thiophene/hydrocarbon distribution in the naphthas herein treated is such that an overhead fraction may be separated containing a major portion of the C_5 and C_6 hydrocarbons, including cyclohexane and methyl cyclopentane as well as like-boiling olefins, while the sulfur compounds recovered in said fraction are typically 85–99 mole-percent mercaptans. In the original cracked naphtha, the thiophene type compounds usually predominate, making up from about 50–90 mole-percent of the total sulfur. Fortuitously, the particular desulfurization process herein described is well adapted for the selective hydrocracking of thiophene-type compounds. This is an important consideration, because 1% by weight of thiophene sulfur may correspond to about 5–10 volume-percent of the liquid feed. By catalytic hydrocracking, the valuable hydrocarbon residues of the thiophene compounds are preserved in the feed thereby increasing the liquid yield. The lower mercaptans which go to the caustic extraction step however generally make up a negligible proportion by volume of the feed, and hence their removal by caustic washing does not significantly lower the liquid yield.

It has been found that from about 10% to 25% by volume of the cracked naphtha feedstock may be successfully fractionated overhead, having an end boiling

point of about 160°–200° F., and still be substantially free of thiophene sulfur, on a debutanized basis. This overhead product, which may initially contain as much as 1.0% of total sulfur by weight may then be treated by solvent extraction, with for example caustic-methanol-water, to produce an essentially doctor sweet product containing 0.0005% of mercaptan sulfur or less, and from about 0.01% to 0.08% of total sulfur. The original naphtha feedstock may contain from about 0.2% to 3% by weight of total sulfur. By extracting the overhead with caustic-methanol-water, a sweetened product is obtained in about 99% liquid yield, having an octane rating of about 95–100 (plus 3 ml. TEL). The same fraction subjected to catalytic reforming under conditions herein described would give about the same liquid yield of a product having an octane number of 85–90 (plus 3 ml. TEL).

The details of the processing may be more readily comprehended in connection with the accompanying flowsheet which illustrates one specific modification for carrying out the process. However, it is not meant to exclude other modifications.

The initial feedstock, comprising for example a high-sulfur, reduced crude oil is preheated to a suitable coking temperature, and admitted via line **1** to a thermal coker **2**, of any suitable conventional design for converting petroleum oils to gases and vapors boiling below a particular end point and producing a solid residue of coke. Such coking unit may be of the delayed coking type wherein coke is accumulated during a coking period of 15 minutes to 2 hours, for example, and is then removed by suitable means such as with a stream of high velocity water. In such cases coker **2** represents one of several coking units which are employed in sequence for coking and decoking whereby a continuous flow of feed and products may be maintained. In another modification coker **2** may be of the continuous type wherein the oil is continuously passed through a bed of heated pellets of coke or other solid heat transfer material, thereby depositing a layer of coke upon such pellets. In general such coking operations are effected at relatively low pressures such as in the range of atmospheric to 100 p.s.i.g., while temperatures may range between about 800° and 1100° F.

Coke is removed from the coker **2** through line **3**. The coker distillate is removed through line **4**, whence it is condensed, and passed into a stabilizer-fractionater **5**, wherein light gases including methane, ethane and propane are removed overhead through line **6** for any desired subsequent utilization. The bottoms from stabilizer **5** are then transferred via line **7** to a naphtha-fractionating column **9**. Fractionating column **9** discharges gasoline-boiling range material, having an end boiling point between about 380° and 460° F. through line **10**. Coker gas-oil is taken off as bottoms through line **11**, and preferably transferred to a thermal cracking unit **12**, which is operated under sufficient temperature and pressure to effect at least a partial cracking of the heavy gas-oil flowing therethrough. Normally, a substantial additional yield of gasoline may be obtained by subjecting the coker gas-oil to thermal cracking. The products from the thermal cracker are then taken off through line **13**, and admitted to a stabilizer-fractionater **14** from which light gases are taken overhead via line **15**. The bottoms product is then transferred via line **17** to naphtha fractionating column **18**.

The gasoline boiling range stock from the cracking operation is withdrawn overhead from fractionating column **18** through line **19**, and is blended with the coker naphtha in line **10**. The combined stream then flows through line **20** into a dehexanizer column **21**. The feed stream admitted to column **21** through line **20** will normally have an initial boiling point of around 75°–85° F., and an end boiling point between about 380°–460° F.

In dehexanizer column **21** the critical separation of thiophene-free overhead from C_5–C_6-lean bottoms is accomplished. This column is ordinarily maintained at atmospheric pressure but slightly reduced or superatmospheric pressures may be employed. The factors of reflux ratios, theoretical plates and feed throughput should be so adjusted as to take overhead at least the major part of all the hydrocarbon components and mercaptans having a true boiling point below about 180° F., while excluding therefrom substantially all compounds containing a thiophene ring, and substantially all hydrocarbon components having a true boiling point above about 190° F. The term "true boiling point" is well understood in the art as referring to the boiling point of an individual component in the absence of vapor pressure-altering contaminants such as azeotrope formers and the like. To obtain the specified fractionation, column **21** may contain between about 10 and 60 actual plates, and overhead reflux ratios of between about 1 and 15 may be employed, these factors being interrelated and balanced against the feed throughput, as will be understood by those skilled in the art.

The overhead from column **21** is much richer in olefins than the original feed. The overhead may contain for example between about 30% and 60% by volume of olefins, where the feed contained only 15–40%. These olefinic compounds appear to display more tendency to azeotrope with like-boiling paraffins and naphthenes than with the thiophene compounds, as evidenced by the substantial absence of thiophene-ring compounds in the overhead. The complexity of the overhead may be appreciated when it is considered that the actual ASTM boiling range is ordinarily from about 80° to 180° F.

The overhead from column **21** is then transferred via line **23** to a debutanizer column **24** wherein a 90–100% butane stream is removed overhead via line **25**. The bottoms from debutanizer **24**, constituting valuable high anti-knock light ends from the gasoline, is then transferred via line **26** to a caustic washing column **27**. Additional feed streams may also be included, as for example a light straight-run fraction admitted through line **58**. The object of treatment in column **27** is to reduce the mercaptan sulfur to the doctor sweet level, and for this purpose, aqueous caustic scrubbing alone is generally insufficient; the addition of a solutizer is ordinarily required as for example methanol, ethanol, butanol, phenols, cresols or the like. The light gasoline stream enters the bottom of column **27** and flows upwardly countercurrently to a stream of aqueous methanol containing sodium hydroxide. The methanol component is preferably admitted to the column at a mid-point therein via line **28**, and the aqueous caustic is preferably admitted near the top of the column through line **29**. By admitting the methanol-free caustic near the downstream end of the column, any methanol which is dissolved in the gasoline is scrubbed therefrom and flows downwardly along with the aqueous caustic and dissolved mercaptides. The operation of such caustic scrubbing columns containing a solutizer is well understood in the art and hence need not be described in detail.

The caustic washed light gasoline is then taken off overhead through line **30**, washed with water admitted through line **31** to a mixing valve **32**, and then admitted to a settling tank **33**. Wash water containing traces of alkali is withdrawn through line **34**, and the sweetened, light gasoline is then withdrawn through line **35** and sent to a storage tank **36**.

The spent caustic-aqueous-methanol from column **27** is withdrawn from the bottom thereof and transferred via line **37** to a caustic and methanol regeneration unit **38**. The regeneration is conventional and need not be described in detail. It ordinarily involves a distillation to strip out a mixture of methanol, water and mercaptan as overhead, followed by condensation and phase separation to recover the bulk of the mercaptans. The methanol-water phase is usually then scrubbed with the

incoming gasoline feedstock from line 26 to scrub out traces of mercaptan, and the thus-purified methanol-water is then recycled to column 27 via line 28. The aqueous caustic, stripped of mercaptans and methanol, is then recycled to the top of column 27 via line 29.

The bottoms from dehexanizer column 21 comprises the primary feedstock which is subjected to catalytic hydrodesulfurization and reforming. This stock contains the great bulk of the refractory thiophene-type sulfur compounds. In order to eliminate such sulfur compounds it is necessary to treat the stock by catalytic hydrodesulfurization. To accomplish this the bottoms fraction in line 72 is admixed with recycle hydrogen from line 73, heated in preheater 39 to desulfurization temperatures, and passed via line 40 to catalytic desulfurizer 41, through which it flows in intimate contact with the cobalt-molybdate catalyst. The preferred reaction conditions in desulfurizer 41 include temperatures between about 625° and 875° F., pressures between about 200 and 5,000 p.s.i.g., hydrogen rates between about 200 and 5,000 s.c.f. per barrel of feed, and space velocities between about 0.5 and 20. The reactions occurring in desulfurizer 41 include the selective hydrocracking of sulfur compounds, nitrogen compounds, oxygen compounds, as well as a substantial saturation of the olefins present therein. There is ordinarily a net consumption of hydrogen amounting to between about 50 and 500 s.c.f. per barrel of feed.

The product from desulfurizer 41 is withdrawn through line 42 and admitted to a high pressure separator 43 from which recycle hydrogen gas is withdrawn through line 44. The liquid product from high pressure separator 43 is then transferred via line 45 to a low pressure separator 46 where dissolved light gases are flashed off through line 47 for use as fuel gas or otherwise as may be desired. The liquid product from separator 46 then constitutes the primary feedstock for the reformer, and is sufficiently low in sulfur that it may be treated with such sulfur-sensitive reforming catalysts as platinum-alumina, or platinum-silica, where the silica has been partially deactivated by steaming or otherwise, or other transitional metal catalysts.

In the particular modification illustrated, the desulfurized product from separator 46 is transferred via line 48 to an intermediate fractionating column 49 wherein a heavy bottoms product constituting a refined stove oil is taken off through line 50. The overhead from column 49 ordinarily has a boiling range from about 150°–400° F., and this product is transferred via line 62 to reformer feed preheater 51, in admixture with recycle hydrogen admitted through line 52. The preheated feed-plus-hydrogen is admitted through line 53 and flows downwardly in contact with the catalyst in reformer 54. The preferred catalyst in reformer 54 is platinum-alumina, i.e. activated alumina containing supported thereon about 0.1% to 1.0% by weight of platinum. Small amounts of chlorine or fluorine may also be included on the catalyst. Other reforming catalysts may be employed as for example, chromia, nickel, cobalt-molybdate, rhodium, molybdena and the like. All of these materials are ordinarily supported on an adsorbent carrier such as activated alumina, alumina-silica, various acid-treated clays, or the like. Normally, the reforming conditions include temperatures between about 850° and 1100° F., pressures between about 100 and 2000 p.s.i.g., hydrogen rates between about 500 and 10,000 s.c.f. per barrel of feed, and space velocities between about 0.5 and 10. These conditions effect substantial dehydrogenation of naphthenes to aromatics, isomerization of paraffins and olefins, cyclization of paraffins and perhaps other reactions, all resulting in increased anti-knock value of the product.

The effluent from reformer 54 is then withdrawn through line 55 and admitted to a high pressure separator 56. Recycle hydrogen gas from the reformer is recycled via lines 57 and 52 to the reformer unit. Inasmuch as the reforming operation results in a net make of hydrogen, the excess is bled off through line 73 and utilized in the hydrogen-consuming desulfurization reactor 41. It is desirable to maintain a hydrogen balance in the process, whereby sufficient hydrogen is synthesized in the reformer to balance the hydrogen consumption in the desulfurizer. To accomplish this objective, sufficient straight-run gasoline feedstock, obtained for example as bottoms from fractionating column 60, is admitted via line 61 to the desulfurizer feed line 72. The straight-run gasoline is high in naphthenes and low in olefins, and hence consumes little hydrogen in the desulfurizer and synthesizes a disproportionately large amount in the reformer. By suitably adjusting the quantity of straight-run gasoline admitted through line 61, in proportion to the cracked stock in line 72, it is possible to maintain the desired hydrogen balance.

The removal of the highly olefinic, highly hydrogen-consuming, light ends in dehexanizer column 21, has a substantial beneficial effect on the overall hydrogen balance maintained in the reformer-desulfurizer combination. This is especially important to refiners whose refinery balance must embrace the disposition of large quantities of high-sulfur, heavy crude oils, and hence thermally cracked gasolines, and wherein there is a limited supply of straight-run gasoline. In many instances, the thermally cracked gasolines available (which must be subjected to hydrodesulfurization before they can be successfully reformed into high octane naphthas) require the consumption of more hydrogen than the available straight-run stocks will generate by reforming. The elimination of the highly olefinic overhead, and its treatment by caustic washing, hence accomplishes the dual objective of preserving the valuable anti-knock qualities of the olefins contained therein, as well as reducing the hydrogen demand in the desulfurizer, thereby giving greater flexibility in the refinery balance, and permitting the treatment in desulfurizer 41, reformer 54, and caustic scrubber column 27, of a larger overall quantity of cracked naphtha feedstock than could be processed through the desulfurizer-reformer combination alone, using only the hydrogen available from reforming a given quantity of straight run gasoline. Even though the net hydrogen make from the reformer is not employed exclusively in the naphtha desulfurizer, it is desirable to minimize hydrogen consumption in the desulfurizer, whereby any excess hydrogen from the reformer may be utilized for other purposes, as e.g. ammonia synthesis or desulfurization of other feedstocks. In some cases, the use of straight-run stocks in the reformer may be eliminated altogether, the desulfurization and reforming reactions being in hydrogen balance as a result of the removal of the highly hydrogen-consuming light ends from the feed.

The desulfurized, reformed, high-octane gasoline in separator 56 is transferred via line 65 to a low pressure separator 66, wherein light gases are flashed off through line 67 for use as fuel or otherwise. The final gasoline product is withdrawn through line 68 and transferred to storage tank 69. The gasoline product in storage tank 69 has high anti-knock quality, but is deficient in light ends required for adequate warm-up quality. Hence, the final gasoline is produced by blending suitable proportions of the light, desulfurized olefinic stock from storage tank 36 via line 70, and the final gasoline blend is transferred to ultimate tankage and storage via line 71.

The cobalt-molybdate catalyst employed in desulfurizer 41 comprises a mixture of cobalt and molybdenum oxides wherein the molecular ratio of CoO to MoO_3 is between about 0.4 and 5.0. This catalyst may be employed in unsupported form or, alternatively, it is preferably distended on a suitable carrier such as alumina, silica, zir-

conia, thoria, magnesia, titania, or any combination thereof. Of the foregoing carriers it has been found that the preferred carrier material is alumina, and especially alumina containing about 3–8% by weight of silica. The supported catalyst may be prepared by impregnation with suitable soluble salts of cobalt and molybdenum followed by drying and calcining, or by coprecipitation or co-pilling methods. Suitable methods for preparing the catalysts are more specifically described in U.S. Patents 2,369,432; 2,325,033; 2,486,361; 2,687,381; 2,393,288 and 2,499,255.

While cobalt-molybdate catalysts are preferred, other desulfurization catalysts may also be employed as for example molybdenum oxide, tungsten oxide, nickel oxide, tungsten-nickel sulfides, or in general any of the transitional metal oxides or sulfides which are capable of effecting the selective hydrocracking of sulfur compounds with concomitant olefin hydrogenation under the conditions herein described. The following example is cited to illustrate the results obtainable in a typical process utilizing a refining sequence similar to that described in connection with the drawing. This example is illustrative only and is not to be construed as limiting in scope.

Example

About 20,000 barrels per day of a Santa Maria Valley (California) crude oil containing 5.0% by weight of sulfur, 0.63 weight percent nitrogen, and having an API gravity of 15 is subjected to delayed thermal coking whereupon there is produced 16,000 barrels of coker distillate, and 500 tons of coke. The coker distillate is fractionated to recover the 450° F. end-point pressure distillate, and the gas-oil residue is subjected to thermal cracking. The thermally cracked product is then fractionated to recover an additional quantity of 450° F. end-point pressure distillate. The combined stream of coker pressure distillate and thermal pressure distillate, containing 1.59% by weight of sulfur, is then carefully fractionated at an over-head true-boiling-point cut point of 185° F., to obtain an overhead amounting to about 23% by volume of the feed to the column. This overhead contains about 40% by volume of olefins, and after debutanizing, has an ASTM boiling range of 110°–180° F., and contains 0.46% by weight of total sulfur.

The debutanized C_5–C_6 fraction is then subjected to countercurrent scrubbing with caustic-aqueous-methanol, and finally with aqueous caustic, yielding 1950 barrels of light gasoline containing 0.04% by weight of total sulfur and 0.0002% of mercaptan sulfur, and having an F–1 leaded (plus 3 ml. TEL) octane rating of about 96. Had this fraction been subjected to catalytic hydrodesulfurization and reforming, its leaded octane rating would be reduced to about 88.

The bottoms product from fractionation of the combined pressure distillates, having a boiling range of 200°–450° F. is then subjected to desulfurization at about 800° F. and 1500 p.s.i.g., with the addition of 3,000 S.C.F. of hydrogen per barrel of feed. The feedstock to the desulfurizer contains about 1.82% sulfur by weight. A liquid feed rate of about 1 volume per volume of catalyst per hour is employed.

The catalyst is a cobalt molybdate type consisting essentially of 2% by weight of CoO and 10% by weight of MoO_3 supported on 5% SiO_2—95% Al_2O_3, the carrier in coprecipitated form. The dried SiO_2—Al_2O_3 cogel is impregnated first with an ammoniacal ammonium molybdate solution, dried, heated to 1200° F. for 2 hours, impregnated secondly with an aqueous solution of cobalt nitrate, dried and heated to 1200° F. for 2 hours.

The effluent from the desulfurizer is then fractionated to recover a desulfurized light product boiling between about 160°–380° F. and containing about 0.005% sulfur. This product is mixed with about 20% by volume of straight-run gasoline of 400° F. end point, and the mixture is supplied to the catalytic reformer operating at about 950° F., a pressure of 450 p.s.i.g., recycle hydrogen rates of about 4000 s.c.f. per barrel of feed, and at a feed rate of about 2.5 volumes of charge per volume of catalyst per hour. The catalyst is activated alumina containing 0.2% by weight of impregnated platinum. Approximately 8,220 barrels of gasoline per day is produced from the reformer, about 6,850 barrels of which is derived from the cracked stock supplied to the desulfurizer. By blending the caustic extracted light gasoline with the reformate gasoline, 10,170 barrels per day of full-range, doctor-sweet gasoline is obtained having a leaded octane rating of 97.3, and containing less than 0.01% sulfur.

By omitting the fractionation step, and sending the light ends of the gasoline through the desulfurizer and reformer under the conditions of this example, substantially the same ultimate liquid yield of gasoline is obtained, wherein however the leaded octane rating is about 95.4. To compensate for this octane loss, more severe reforming conditions could be employed, but the liquid yield is then about 2.0% less, resulting in an ultimate recovery of 9,967 barrels of gasoline of 97.3 leaded octane rating.

The foregoing example may be modified by employing different catalysts at substantially the same reaction conditions, or the reaction conditions may be modified using the same catalysts to obtain the same results. The foregoing disclosure is hence not to be considered as limiting since many variations may be made by those skilled in the art without departing from the scope or spirit of the following claims.

I claim:

1. A process for desulfurizing and reforming a full-range, high-sulfur, thermally cracked naphtha, which comprises fractionating said naphtha to recover a light overhead fraction rich in olefins and a heavy bottoms fraction constituting substantially the entire remainder of said naphtha, said light fraction containing the major part of all the hydrocarbon components and mercaptans having a true boiling point below about 180° F., said light fraction being substantially free from (1) compounds containing a thiophene ring and (2) hydrocarbon components having a true boiling point above about 190° F., subjecting said light fraction to aqueous- alkaline extraction to extract therefrom said mercaptans, subjecting said heavy fraction to catalytic hydrodesulfurization in the presence of hydrogen and a cobalt molybdate catalyst at temperatures between about 625° and 875° F., subjecting the desulfurized heavy fraction to catalytic reforming in the presence of hydrogen and a reforming catalyst comprising as an essential element an active metal selected from groups VIB and VIII of the periodic table, and thereafter blending portions of the reformed heavy gasoline from said reforming step with a portion of said caustic-washed light fraction to obtain a desulfurized full-range gasoline of higher anti-knock quality than would be produced by subjecting said full-range cracked naphtha to hydrodesulfurization and reforming under the same conditions.

2. A process as defined in claim 1 wherein sufficient straight-run gasoline is included with said desulfurized heavy fraction supplied to said reformer to generate therein sufficient hydrogen to balance the hydrogen consumed in said hydrodesulfurization step, and sufficient of said generated hydrogen is passed to said hydrodesulfurization to supply the hydrogen therein consumed.

3. A process as defined in claim 1 wherein said reforming catalyst is activated alumina containing a minor proportion of platinum.

4. A process for desulfurizing and reforming a full-range, high-sulfur, thermally cracked naphtha, which comprises fractionating said naphtha to recover a light overhead fraction rich in olefins and a heavy bottoms fraction constituting substantially the entire remainder

of said naphtha, said light fraction containing the major part of all the hydrocarbon components and mercaptans having a true boiling point below about 180° F., said light fraction being substantially free from (1) compounds containing a thiophene ring and (2) hydrocarbon components having a true boiling point above about 190° F., subjecting said light fraction to aqueous-alkaline extraction to extract therefrom said mercaptans, subjecting said heavy fraction to catalytic hydrodesulfurization at a temperature between about 625° and 875° F. in the presence of hydrogen and a catalyst selected from the group consisting of the oxides and sulfides of the transitional metals, subjecting the desulfurized heavy fraction to catalytic reforming in the presence of hydrogen and a reforming catalyst comprising as an essential element an active metal selected from groups VIB and VIII of the periodic table, and thereafter blending portions of the reformed heavy gasoline from said reforming step with a portion of said caustic-washed light fraction to obtain a desulfurized full-range gasoline of higher anti-knock quality than would be produced by subjecting said full-range cracked naphtha to hydrodesulfurization and reforming under the same conditions.

5. A process for refining a heavy crude oil rich in sulfur compounds which comprise passing said crude oil into a coking zone maintained at a temperature between about 800° and 1100° F. wherein said crude oil is converted to coke, gases, and a coker distillate having an increased ratio of hydrogen to carbon, separating a naphtha fraction and a higher boiling fraction from said coker distillate, passing said higher boiling fraction through a thermal cracking zone, withdrawing cracked products from said thermal cracking zone, separating from said cracked products a naphtha fraction and a higher boiling fraction, combining said coker distillate naphtha with said thermally cracked naphtha, subjecting the combined naphthas to fractional distillation to recover a light overhead fraction rich in olefins and a heavy bottoms fraction constituting substantially the entire remainder of said combined naphthas, said light fraction containing in major part of all the hydrocarbon components and mercaptans having a true boiling point below about 180° F., said light fraction being substantially free from (1) compounds containing a thiophene ring and (2) hydrocarbon components having a true boiling point above about 190° F., subjecting said light fraction to aqueous-alkaline extraction to extract therefrom said mercaptans, subjecting said heavy fraction to catalytic hydrodesulfurization in the presence of hydrogen and a cobalt molybdate catalyst at a temperatures between about 625° and 875° F., subjecting the desulfurized heavy fraction to catalytic reforming in the presence of hydrogen and a platinum reforming catalyst, and thereafter blending portions of the reformed heavy naphtha from said reforming step with a portion of said caustic-washed light fraction to obtain a desulfurized full-range naphtha of higher anti-knock quality than would be produced by subjecting said combined full-range cracked naphthas to hydrodesulfurization and reforming under the same conditions.

6. A process as defined in claim 5 wherein sufficient stright-run gasoline is included with said desulfurized heavy fraction supplied to said reformer to generate therein sufficient hydrogen to balance the hydrogen consumed in said hydrodesulfurization step, and sufficient of said generated hydrogen is passed to said hydrodesulfurization to supply the hydrogen therein consumed.

7. A process as defined in claim 5 wherein said cobalt molybdate catalyst is supported on a carrier consisting of activated alumina containing a minor proportion of coprecipitated silica.

8. In a combined catalytic desulfurization and catalytic reforming process, wherein a thermally cracked naphtha is first subjected to hydrogenative desulfurization in the presence of a cobalt molybdate catalyst, and thereafter subjected to dehydrogenative reforming in the presence of a platinum-alumina catalyst, and wherein the hydrogen consumed in said desulfurization reaction is derived exclusively from said reforming step, and whenein an amount of straight-run gasoline is supplied to said reforming zone sufficient only to generate a net hydrogen make sufficient to supply the hydrogen consumption in said desulfurization reaction, the improved method of minimizing hydrogen consumption in the desulfurization reaction and thus the amount of straight-run gasoline which must be supplied to said reforming zone, which comprises first separating from the full-range cracked naphtha supplied to said desulfurization zone a highly olefinic light fraction boiling substantially within the range of about 80°–180° F., said light fraction being substantially free from compounds containing a thiophene ring, subjecting said light fraction to scrubbing with an aqueous caustic solution to extract mercaptans therefrom without affecting the olefins contained therein, and reblending the sweetened light gasoline from said caustic scrubbing step with the reformed gasoline from said reforming step.

9. A process as defined in claim 8 wherein said cracked naphtha comprises a coker distillate boiling between about 80° and 450° F.

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