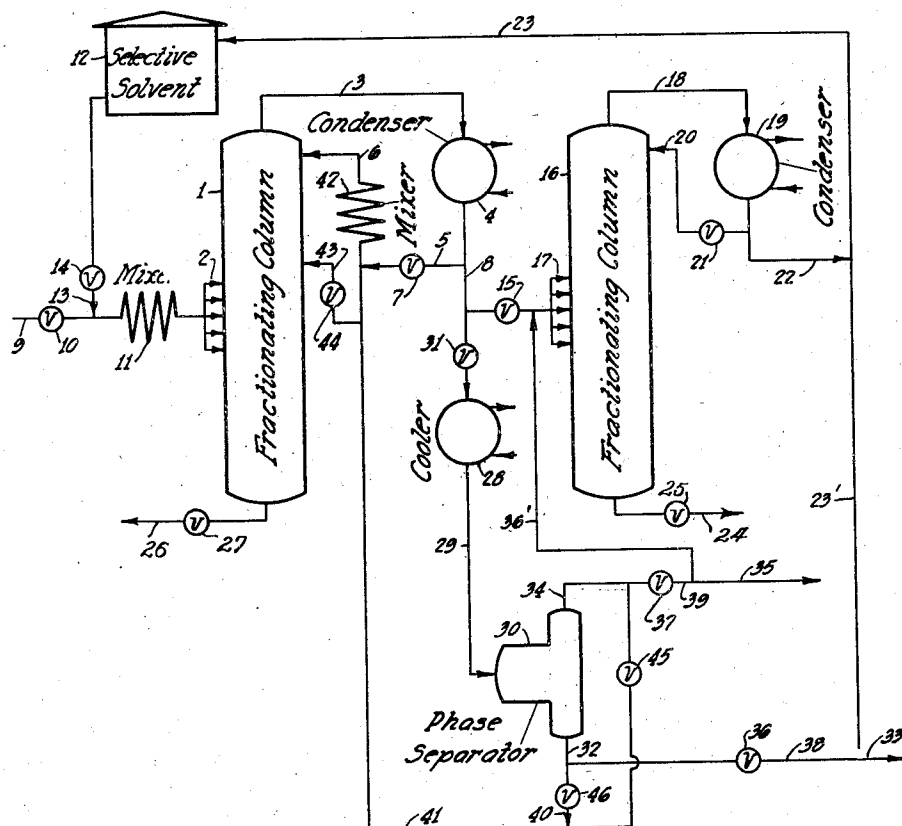


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PROCESS OF REFINING OILS
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PROCESS OF REFINING OILS

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This invention relates to the treating of hydrocarbon products and is particularly concerned with a process for removing sulfur compounds from hydrocarbon oils such as gasoline, kerosene, naphthas, solar oils, fuel oils, etc., which may be either straight run distillates or cracked distillates, and may be derived from petroleum crudes, fractions of coal tar, or brown coal tar, and mixtures obtained by the hydrogenation of carbonaceous substances.

It has heretofore been found to be impractical and generally impossible to separate sulfur compounds from hydrocarbon mixtures by fractional distillation because the sulfur compounds have the same boiling ranges as valuable hydrocarbons contained in the fraction. The common practice in the art comprises subjecting sulfur-bearing distillates to chemical treatments which convert some sulfur compounds to other compounds which may be more readily removed by simple chemical or physical methods, and/or which are less obnoxious. Certain other sulfur compounds are in this manner converted only at often prohibitive expenditures of chemicals and losses of valuable hydrocarbons, while still others are not affected at all. Processes of this type are at times costly and often result in a considerable loss of valuable products.

More recently, a demand for more complete utilization of the natural petroleum and similar products resulted in the treatment of hydrocarbon mixtures which are very difficult to treat. The cracked distillates are particularly difficult to refine by ordinary methods on account of their relatively high sulfur content, the sluggish response of some of these sulfur compounds to refining processes, and the presence in the cracked distillates of unsaturated hydrocarbons which are more reactive with the chemicals intended for sulfur removal, and thus decrease the effectiveness of treatment and increase the treating losses.

It is an object of my invention to provide a distillation process for separating at least a portion of the sulfur compounds from hydrocarbons, which process may supplement or be used instead of a chemical treatment for removing sulfur compounds from oil or converting them into different substances. It is a further object of my invention to provide an efficient and flexible method for reducing the sulfur content of a hydrocarbon oil, and especially the oils which cannot be satisfactorily treated by conventional methods. It is a further object of my invention to provide a process for fractionating a sulfur-bearing hydrocarbon oil which will produce a distillate having

a materially lower sulfur content than the original oil.

I have discovered that by distilling hydrocarbon fractions containing sulfur compounds in the presence of polar substances which are preferential solvents for the sulfur compounds, a distillate can be produced which contains substantially reduced quantities of sulfur and is often substantially free from sulfur. The sulfur compounds are thereby concentrated in the residue or bottom products of the distillation process. After the main fractionation the polar substance may be recovered from each of the distillation products, and reused in the further treatment of hydrocarbon distillates, thereby effecting a saving in the consumption of chemicals required in removing sulfur compounds from the hydrocarbons.

I have found that it is often economical to employ a combination of treatments, comprising the distillation of a hydrocarbon fraction with a polar selective solvent to produce a distillate containing reduced amounts of sulfur, and the removal or conversion of the residual sulfur in the distillate by other methods, such as treatment with sulfuric acid, plumbite, or alkali, distillation with a metallic acetate, such as copper acetate, followed by a treatment with absorptive material, etc.

Moreover, I have found that my process may be operated more efficiently, i. e., so as to improve the purity of the sulfur compounds which are obtained in the bottom product, by fractionating in the manner disclosed in my copending application Serial No. 12,007 filed March 20, 1935.

According to this mode of operation, the ratio of desirable hydrocarbons to the solvent in the top product is maintained equal to the ratio of these substances in the feed. This may be effected according to either of the following modes of operation:

a. The overhead mixture, or a portion thereof, is treated to withdraw therefrom a top product containing the solvent and the hydrocarbons in the same ratio as they occur in the feed, and the remaining portion of the overhead mixture is returned to the column, either with the reflux, or separately at another level in the column. A convenient method of withdrawing this top product from the overhead mixture consists in chilling the portion of the overhead which is to be treated so as to cause it to stratify into two liquid phases of different composition, i. e., into two portions which are relatively richer and poorer in hydrocarbons, separating these phases, as by decantation, withdrawing therefrom such quantities as

are required to produce a top product of the desired composition, and returning the residual portion of the overhead mixture to the column. It is not always practical to cause the separation of the formation of two layers by chilling the condensate. In these cases the separation of the condensate into two layers can often be accomplished by adding water or another similar chemical to the overhead mixture or to the condensate.

b. The ratio of the solvent and the initial sulfur-bearing hydrocarbon mixture is so controlled as to produce a feed composition which contains the solvent and the hydrocarbons in the same ratio as they occur in the overhead mixture, which is then withdrawn from the system as top product.

This desired balance between the feed and the top product is increasingly more difficult to achieve as the boiling range of the initial fraction increases, since in multi-component systems containing large numbers of hydrocarbons, it is not practically possible to obtain an overhead mixture which contains all of the many different hydrocarbons in the same concentrations as they occur in the sulfur-bearing feed. The principle of adjusting the feed and overhead composition can, however, be applied to such systems to a sufficient degree of approximation to achieve a material increase in the efficiency of my process.

It is, therefore, possible in practice to obtain a bottom product which is rich in sulfur compounds, and which contains very little or no solvent and/or hydrocarbons by properly controlling the composition of the top product and/or of the feed. The concentration of the sulfur compounds will further depend upon the degree of rectification effected in the distillation column.

It is not always possible to maintain the top product and feed compositions in the exact relation described above throughout an entire fractionation, and it is, therefore, often necessary to deviate slightly from the ideal equality of ratios. I prefer in these cases to operate in a manner to cause the deviation to be such that the ratio of the hydrocarbon to the solvent in the top product is greater than this ratio in the feed, rather than to cause the said ratio to be smaller. The effect of a deviation in this direction is to produce a bottom product containing substantially only sulfur compounds and a small amount of solvent, but none or substantially reduced concentration of hydrocarbons. Since in most cases it is easy to separate the solvent from the sulphur compounds in the bottom product, this deviation is preferred to one in the other direction according to which larger amounts of hydrocarbons occur in the bottom product.

The above described modes of controlling the top product composition or of adjusting the amount of the solvent in the feed mixture normally necessitates frequent analyses of the top product, which is often inexpedient. I have found that in practice these analyses can generally be avoided by an experienced operator by observing the temperature which obtains in the fractionating column. If the column is provided with several temperature indicating devices at different levels, it is preferable to select one at which the temperature changes, and to note the proper temperature when the proper operation prevails. With constant operating conditions a variation in the temperature at this level will immediately apprise the operator that the compositions must be changed.

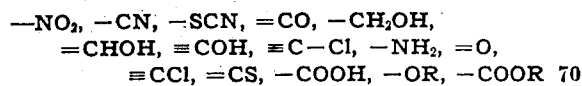
I have further found that improved results are

sometimes obtained by initially distilling the material to be treated into a number of narrower-boiling fractions, and subjecting one or more fractions separately to my desulfurization treatment, either with or without resort to the feature of adjusting the feed and top product compositions. By a foresighted selection of boiling ranges of the fractions it is often possible to isolate certain fractions requiring no treatment, and/or which may be treated by ordinary methods, and to fractionate only those fractions which are difficult to desulfurize by ordinary methods because they contain sulfur compounds in increased concentrations or of such a nature that they are sluggish in their response or non-responsive to ordinary refining methods. I have found that the fractions which contain thiophene and thiophene derivatives, such as thiotolene, thioxene and other thiophene analogues and/or homologues are the most difficult to treat by ordinary methods, and my invention is especially applicable to the treatment of these fractions. These sulfur-bearing fractions may have boiling ranges from about 100° C. to about 300° C., although some times there exist certain smaller intermediate fractions falling within this range which are largely free from these sulfur compounds.

Another purpose of this preliminary distillation is to effect an increased efficiency of the process of my invention. Thus, I have found that if the fractions treated having boiling ranges which are not substantially greater than 30° C. or 80° C., I am, in some cases, able to obtain a much sharper separation, whereby both the quantity of sulfur compounds in the distillate and the quantity of hydrocarbons in the bottom product are greatly reduced.

It is preferable to use a solvent having a boiling point which is sufficiently low to cause a mixture of said solvent and the highest boiling hydrocarbon of the mixture to boil at a temperature below the lowest boiling sulfur compounds to be removed. It is, therefore, possible to use solvents boiling at temperatures below the boiling range of the fraction, or at temperatures falling within or even above the said range, provided that the solvent and the hydrocarbons form low boiling mixtures which boil below the lowest boiling sulfur compound, or sufficiently low to produce a final product of a desired sulfur content. While my process may be employed to cause the removal of substantially all of the sulfur, it is also practiced when the sulfur content is merely lowered and a portion of the sulfur is retained in the final product.

I may employ any solvent which has the above described boiling temperature characteristics, and which is a selective solvent for the sulfur compounds. I may use organic polar liquids of the type used in the liquid solvent extraction of hydrocarbon mixtures to effect a separation between aromatic and paraffinic hydrocarbons, or between hydrocarbons of different degrees of saturation such as organic compounds, either aliphatic, carbocyclic, or heterocyclic, containing one or more of the following groups:



where R designates an alkyl radical, which may be either aliphyl or aryl. Examples of these solvents are: Nitrobenzene, benzonitrile, monochloroacetonitrile, phenyl thiocyanate, phenolthiocyanate, formate of pyridine, benzaldehyde, ace-

tone, furfural, furfuryl alcohol, chlorisopropyl alcohol, diacetone alcohol, aniline methyl lactate, triacetin, diacetin, methyl nitrobenzoate, formic acid, ethylenechlorhydrin, glycol monoacetate, glycol diacetate, lactic acid nitrile, 5
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pyridine, chlorophenol, etc. My invention is not, however, limited to the specific solvents enumerated, nor to solvents containing the enumerated chemical groups, but may be used with any selective solvent for sulfur compounds. My invention is not concerned with distillation processes employing immiscible liquids, like water, and described in the British Specification No. 365,571.

I have, however, found that superior results can be obtained by employing the following substances as solvents, and they constitute the preferred form of my invention: Furfural, aniline, methyl cyanide, ethylene diamine, nitromethane and acetic anhydride.

The mode of operation may be more fully understood by referring to the accompanying drawing showing a schematic form of apparatus and a flow diagram which may be utilized in connection with the invention, it being understood that the specific details and arrangements illustrated are exemplary only.

In the drawing, 1 is a fractional distillation column, provided with an intake manifold 2, overhead takeoff 3, reflux condenser 4, and reflux lines 5 and 6. A valve 7 may be provided to regulate the quantity of reflux, and may, if desired, be operated automatically, as by a flow controller, a thermostat or a pressure responsive device located in the fractionating column 1. The top product may be withdrawn at 8 from condensate of the condenser 4, or a separate top product takeoff may be provided. Heaters, heat exchangers, pumps, gauges, and other auxiliary equipment, not shown, may be provided.

A feed mixture of hydrocarbons and sulfur compounds flows through a conduit 9 and valve 10, and is mixed in a mixing device 11 with a suitable selective solvent introduced from a storage 12 through a conduit 13 and valve 14, and fed into the fractionating column 1. A portion of the condensate from the condenser 4, consisting of hydrocarbons containing no sulfur or substantially reduced amounts of sulfur, and solvent, is withdrawn through 8 as top product at the proper rate, controlled by a valve 15. The solvent may in certain cases be allowed to remain in the top product, as when it imparts desirable characteristics to the hydrocarbons. If desired, the solvent may be recovered by feeding the top product into a fractional distillation column 16, which may be similar to the column 1, in that it is equipped with an intake manifold 17, an overhead takeoff 18, a reflux condenser 19, and a reflux line 20, controlled by a valve 21. The solvent, in any desired state of purity, may be withdrawn at 22 and returned to storage through a conduit 23, and the hydrocarbons may be recovered at 24 at a rate controlled by a valve 25.

The sulfur compounds may be withdrawn at 26 in a concentrated form as a bottom product of the column 1, at a rate controlled by a valve 27. The quantity of these sulfur compounds is generally very small as compared to the quantity of hydrocarbons distilled, and I have found it to be desirable, but not necessary, to permit the sulfur compounds to accumulate in the bottom of the still, which may be operated either continuously or in a batch operation, and to remove the bottom

product only after a sufficient amount of sulfur compounds has been concentrated to permit the removal as bottoms of a product which is rich in sulfur compounds, and low in hydrocarbons, thereby materially reducing the loss of the desired hydrocarbons. Thus, I may initially close the valve 27 and operate the column 1 until enough sulfur compounds are accumulated in the lower portion of the column 1 to permit the removal of a bottom product which contains the sulfur compounds in a very concentrated form, or until their presence is detrimental to the purity of the overhead mixture. When this stage has been reached I may withdraw the bottom product intermittently, or continuously, at any desired rate, as, for example, at the same rate as the sulfur compounds are fed into the column at 2. In batch operations I may initially run a number of batches and then remove all of the bottoms at once, or may then withdraw after each run only as much sulfur bottoms as was introduced during the preceding run. Similarly, in continuous operations, I may initially operate for the time required to build up the desired sulfur concentration, and then either remove all of the bottoms, or open the valve 27 so as to withdraw a small quantity sufficient to maintain a substantially constant sulfur concentration in the column.

The bottom product from 26 may, if desired, be further fractionated to recover the solvent, if it is present in sufficient quantity to warrant recovery.

If desired, I may reduce the load on the fractionator 16 by first cooling and/or chilling the top product in a cooler 28, and feeding it through a conduit 29 into a decanter, centrifuge, or other suitable phase separator 30, valve 31 being opened the proper amount and valve 15 being closed. The cooler 28 cools the top product to a temperature at which it separates into two liquid phases. Assuming that the phase consisting mainly or totally of the solvent is heavier than the other phase, it is withdrawn at 32, and may be returned to storage through a conduit 23', or taken off at 33 as a separate product. It may be, if desired, further concentrated by any desired method, such as distillation, salting out, extraction, etc., before being returned to the storage 12. The other phase, which is richer in hydrocarbons, may be withdrawn at 34 and taken off as a product at 35, or fed to the fractionating column 16 through a conduit 36'.

As stated above, it is often desirable to maintain the ratio of the hydrocarbons to the solvent in the top product equal to the ratio of these substances in the feed. This control may be realized by either of the following methods of operation:

a. By adjusting the valves 36 and 37 the separated phases from the phase separator 30 can be divided into a top product of the desired composition and quantity, which is withdrawn through the conduits 38 and 39, and, valves 45 and 46 being open, a secondary or added reflux, which is returned to the column 1 through conduits 40 and 41 and introduced either with the main reflux, for instance, after being mixed therewith in a mixer 42, or separately at any desired level in the column, as through a conduit 43, controlled by a valve 44. With substantially constant rate of feed of a sulfur bearing hydrocarbon mixture through the valve 10 and of the solvent through the valve 14, a feed having a constant ratio of hydrocarbons to solvent equal to X is introduced at 2. It should be noted that the liquid flowing through the conduit 13 will often not consist of pure sol-

vent, but may have a composition corresponding to that of the phase withdrawn at 32 and returned through the conduit 23. For the conditions of operation of the column 1, an overhead mixture will be withdrawn at 3 which will contain hydrocarbons and the solvent in a ratio Y, which will not, save in a fortuitous case, equal X. It is, however, desirable that the composite top product withdrawn, i. e., the aggregate of the products flowing through the valves 36 and 37, contain hydrocarbons and solvent in the ratio of X, and that the correct amount of top product be withdrawn. Accordingly, either valve 36 or valve 37, or both, may be opened to the extent necessary to withdraw a top product containing hydrocarbons and solvent in the ratio of X, and the remainder of the phases from the phase separator 30 is returned to the column 1. When this mode of operation is pursued substantially pure sulfur compounds may be recovered at 26, provided, of course, that the column is capable of a sufficient degree of rectification.

It should be noted that it is possible to close valve 7, and to carry all of the reflux through conduits 40 and 41.

b. According to the second mode of operation, the valves 10 and 14 are adjusted so that X, the ratio of hydrocarbons to solvent in the feed at 2 is equal to Y, the ratio of these components in the overhead mixture. In this situation the valves 45 and 46 remain closed and the top product composition is the same as that of the overhead mixture. The top product may, therefore, be fed directly into the column 16 through the valve 15, thereby eliminating the phase separator 30. Or, if desired, the phase separator 30 may be employed to effect the separation of the solvent and the hydrocarbons in the manner described above.

Since many of the selective solvents which are useful in my distillation are preferential solvents for certain components of hydrocarbon oils, it is possible to combine a solvent extraction step with my desulfurizing treatment to produce several portions of hydrocarbons having different solubilities in selective solvents. For example, the hydrocarbons may be separated into portions which are relatively more paraffinic and less paraffinic. Thus, the hydrocarbons withdrawn at 34 are more paraffinic than those which occur in the solvent phase which is withdrawn at 32. It is often possible to further extract the phase flowing through conduit 39 with additional solvent from the tank 12 or with a different solvent, to produce a more paraffinic product.

In operations which do not require the employment of the phase separator 30 to adjust the composition of the top product, I may replace it by a single or multistage countercurrent treater, and may add additional quantities of solvent, if required.

I claim as my invention:

1. The process of refining a hydrocarbon fraction containing sulfur compounds which comprises rectifying the said fraction together with a preferential solvent for the said sulfur compounds in a distillation zone maintaining the conditions of temperature and pressure in said zone to distill at least a substantial portion of the solvent together with refined hydrocarbons, withdrawing from the distillation zone a rectified top product derived from the combined mixture and containing refined hydrocarbons and forming a distillation bottom product in which sulfur compounds are concentrated.

2. In a continuous process of refining a hydrocarbon fraction containing sulfur compounds, the steps of continuously introducing the said fraction and a preferential solvent for the said sulfur compounds into a distilling apparatus, maintaining within the apparatus counterflowing streams of vapors and reflux derived from the combined mixture, maintaining the conditions of temperature, pressure, and reflux in said apparatus to distill at least a substantial portion of the solvent together with refined hydrocarbons, continuously withdrawing from the apparatus a top product containing the refined hydrocarbons and forming a distillation bottom product in which sulfur compounds are concentrated.

3. The process of refining a hydrocarbon fraction containing sulfur compounds which comprises the steps of rectifying the said fraction together with a preferential solvent for the said sulfur compounds in a distillation zone, maintaining the conditions of temperature and pressure in said zone to distill at least a substantial portion of the solvent together with refined hydrocarbons, withdrawing from the distillation zone a rectified overhead mixture derived from the combined mixture and containing the refined hydrocarbons forming a distillation bottom product in which sulfur compounds are concentrated, and separating the solvent from the said overhead mixture.

4. The process of refining a hydrocarbon fraction containing sulfur compounds, which comprises rectifying successive quantities of said fraction together with a preferential solvent for the said sulfur compounds in a distillation zone, maintaining the conditions of temperature and pressure in said zone to distill at least a substantial portion of the solvent together with refined hydrocarbons, withdrawing from the distillation zone a rectified top product derived from the combined mixture and containing the refined hydrocarbons forming a distillation bottom product in which sulfur compounds are concentrated, and withdrawing at least a portion of the bottom product after a number of such quantities of hydrocarbons have been rectified.

5. The process according to claim 4 in which the bottom product is removed in such quantities as to maintain in the distillation zone a hydrocarbon mixture containing sulfur compounds in a concentrated form.

6. The process of refining a hydrocarbon fraction containing sulfur compounds which comprises the steps of rectifying the said fraction together with a preferential solvent for the said sulfur compounds in a distillation zone, maintaining the conditions of temperature and pressure in said zone to distill at least a substantial portion of the solvent together with refined hydrocarbons, withdrawing from the distillation zone a rectified overhead mixture derived from the combined mixture and containing the refined hydrocarbons forming a distillation bottom product in which sulfur compounds are concentrated, condensing and cooling at least a portion of said overhead mixture to cause it to separate into two liquid phases, one of said phases being rich in the said solvent, and the other phase being poor in the said solvent, and withdrawing the latter phase as a top product.

7. The process of refining a hydrocarbon fraction containing sulfur compounds which comprises the steps of rectifying the said fraction together with a preferential solvent for the said sulfur compounds in a distillation zone, main-

maintaining the conditions of temperature and pressure in said zone to distill at least a substantial portion of the solvent together with refined hydrocarbons, withdrawing from the distillation zone a rectified overhead mixture derived from the combined mixture and containing the refined hydrocarbons forming a distillation bottom product in which sulfur compounds are concentrated, condensing and cooling at least a portion of said overhead mixture to cause it to separate into two liquid phases, one of said phases being rich in the said solvent, and the other phase being poor in the said solvent, and removing the solvent from the hydrocarbons in the phase which is poor in solvent to produce a hydrocarbon product.

8. The process of refining a hydrocarbon fraction containing sulfur compounds which comprises the steps of rectifying the said fraction together with a preferential solvent for the said sulfur compounds in a distillation zone, maintaining the conditions of temperature and pressure in said zone to distill at least a substantial portion of the solvent together with refined hydrocarbons, withdrawing from the distillation zone a rectified overhead mixture derived from the combined mixture and containing the refined hydrocarbons forming a distillation bottom product in which sulfur compounds are concentrated, condensing and cooling at least a portion of said overhead mixture to cause it to separate into two liquid phases, one of said phases being rich in the said solvent, and the other phase being poor in the said solvent, and separating the solvent from the hydrocarbons in the phase which is rich in solvent to produce a hydrocarbon product.

9. The process of refining a hydrocarbon fraction containing sulfur compounds which comprises the steps of rectifying the said fraction together with a preferential solvent for the said sulfur compounds in a distillation zone, maintaining the conditions of temperature and pressure in said zone to distill at least a substantial portion of the solvent together with refined hydrocarbons, withdrawing from the distillation zone a rectified overhead mixture derived from the combined mixture and containing the refined hydrocarbons forming a distillation bottom product in which sulfur compounds are concentrated, condensing and cooling at least a portion of said overhead mixture and extracting it in an extraction zone with an additional quantity of the said solvent to produce a raffinate phase which is poor in solvent and an extract phase which is rich in solvent, and separating the said phases.

10. The process of refining a hydrocarbon fraction containing sulfur compounds which comprises introducing a feed mixture containing the said fraction and a preferential solvent for the said sulfur compounds into a distillation zone, maintaining the conditions of temperature and pressure in said zone to distill at least a substantial portion of the solvent together with refined hydrocarbons, withdrawing from the distillation zone a rectified overhead mixture derived from the said feed mixture forming a distillation bottom product in which sulfur compounds are concentrated, withdrawing a portion of the said overhead mixture as a top product and maintaining in the said feed mixture and in the said top product substantially the same ratio of the solvent to the hydrocarbons.

11. The process of refining a hydrocarbon fraction containing sulfur compounds which comprises introducing a feed mixture containing the said fraction and a preferential solvent for the said sulfur compounds into a distillation zone, maintaining the conditions of temperature and pressure in said zone to distill at least a substantial portion of the solvent together with refined hydrocarbons, withdrawing from the distillation zone a rectified overhead mixture derived from the said feed mixture forming a distillation bottom product in which sulfur compounds are concentrated, withdrawing a portion of the said overhead mixture as a top product and controlling the composition relationship between the feed and the top product so that the ratio of the solvent and the hydrocarbons is not substantially greater in the top product than in the feed.

12. The process of refining a hydrocarbon fraction containing sulfur compounds which comprises introducing a feed mixture containing the said fraction and a preferential solvent for the said sulfur compounds into a distillation zone, maintaining the conditions of temperature and pressure in said zone to distill at least a substantial portion of the solvent together with refined hydrocarbons, withdrawing from the distillation zone a rectified overhead mixture derived from the said feed mixture forming a distillation bottom product in which sulfur compounds are concentrated, withdrawing a portion of the said overhead mixture as a top product and adjusting the quantity of the solvent in the feed mixture so that the solvent and the hydrocarbons occur in the feed in substantially the same ratio as they occur in the top product.

13. The process of refining a hydrocarbon fraction containing sulfur compounds which comprises introducing a feed mixture containing the said fraction and a preferential solvent for the said sulfur compounds into a distillation zone, maintaining the conditions of temperature and pressure in said zone to distill at least a substantial portion of the solvent together with refined hydrocarbons, withdrawing from the distillation zone a rectified overhead mixture derived from the said feed mixture, withdrawing a portion of the said overhead mixture as a top product and adjusting the quantity of the solvent in the feed mixture so that the solvent and the hydrocarbons occur in the feed in a ratio which is not substantially less than the ratio in which they occur in the top product.

14. The process of refining a hydrocarbon fraction containing sulfur compounds which comprises introducing a feed mixture containing the said fraction and a preferential solvent for the said sulfur compounds into a distillation zone, maintaining the conditions of temperature and pressure in said zone to distill at least a substantial portion of the solvent together with refined hydrocarbons, withdrawing from the distillation zone a rectified overhead mixture derived from the said feed mixture forming a distillation bottom product in which sulfur compounds are concentrated, condensing and cooling at least a portion of the said overhead mixture to cause it to separate into two liquid phases, withdrawing from the said phases a top product containing the solvent and the hydrocarbons in substantially the same ratio as they occur in the said feed mixture, and returning to the distillation zone the withdrawn overhead mixture less the withdrawn top product.

15. The process of refining a hydrocarbon fraction containing sulfur compounds which comprises introducing a feed mixture containing the said fraction and a preferential solvent for the said sulfur compounds into a distillation zone, maintaining the conditions of temperature and pressure in said zone to distill at least a substantial portion of the solvent together with refined hydrocarbons, withdrawing from the distillation zone a rectified overhead mixture derived from the said feed mixture forming a distillation bottom product in which sulfur compounds are concentrated, condensing and cooling at least a portion of the said overhead mixture to cause it to separate into two liquid phases withdrawing from the said phases a top product containing the solvent and the hydrocarbons in a ratio which is not substantially greater than the ratio in which they occur in the said feed mixture, and returning to the distillation zone the withdrawn overhead mixture less the withdrawn top product.

16. The process according to claim 1 in which the boiling range of the hydrocarbon fraction is not substantially greater than 80° C.

17. The process according to claim 10 in which the boiling range of the hydrocarbon fraction is not substantially greater than 80° C.

18. The process according to claim 1 in which the boiling temperature of the solvent is not substantially above the lower limit of the boiling temperature range of the said fraction at the pressure in the distillation zone.

19. The process according to claim 10 in which the boiling temperature of the solvent is not substantially above the lower limit of the boiling temperature range of the said fraction at the pressure in the distillation zone.

20. The process of refining a hydrocarbon fraction boiling within gasoline range containing sulfur compounds which comprises rectifying the said fraction in a distillation zone together with a solvent from the group consisting of furfural, aniline, methyl cyanide, ethylene diamine, nitromethane and acetic anhydride, maintaining the conditions of temperature and pressure in said zone to distill at least a substantial portion of

the solvent together with refined hydrocarbons, withdrawing from the distillation zone a rectified top product derived from the combined mixture and containing the refined hydrocarbons and forming a distillation bottom product in which sulfur compounds are concentrated.

21. The process of refining a hydrocarbon fraction containing sulfur compounds which comprises rectifying the said fraction in a distillation zone together with methyl cyanide, maintaining the conditions of temperature and pressure in said zone to distill at least a substantial portion of the cyanide together with refined hydrocarbons, withdrawing from the distillation zone a rectified top product derived from the combined mixture and containing the refined hydrocarbons and forming a distillation bottom product in which sulfur compounds are concentrated.

22. The process of refining a hydrocarbon fraction containing sulfur compounds which comprises rectifying the said fraction in a distillation zone together with ethylene diamine, maintaining the conditions of temperature and pressure in said zone to distill at least a substantial portion of the diamine together with refined hydrocarbons, withdrawing from the distillation zone a rectified top product derived from the combined mixture and containing the refined hydrocarbons and forming a distillation bottom product in which sulfur compounds are concentrated.

23. The process of refining a hydrocarbon fraction containing sulfur compounds which comprises rectifying the said fraction in a distillation zone together with nitromethane, maintaining the conditions of temperature and pressure in said zone to distill at least a substantial portion of the nitromethane together with refined hydrocarbons, withdrawing from the distillation zone a rectified top product derived from the combined mixture and containing the refined hydrocarbons and forming a distillation bottom product in which sulfur compounds are concentrated.

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