

June 10, 1969

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3,449,242

DESULFURIZATION PROCESS FOR HEAVY PETROLEUM FRACTIONS

Filed March 15, 1966

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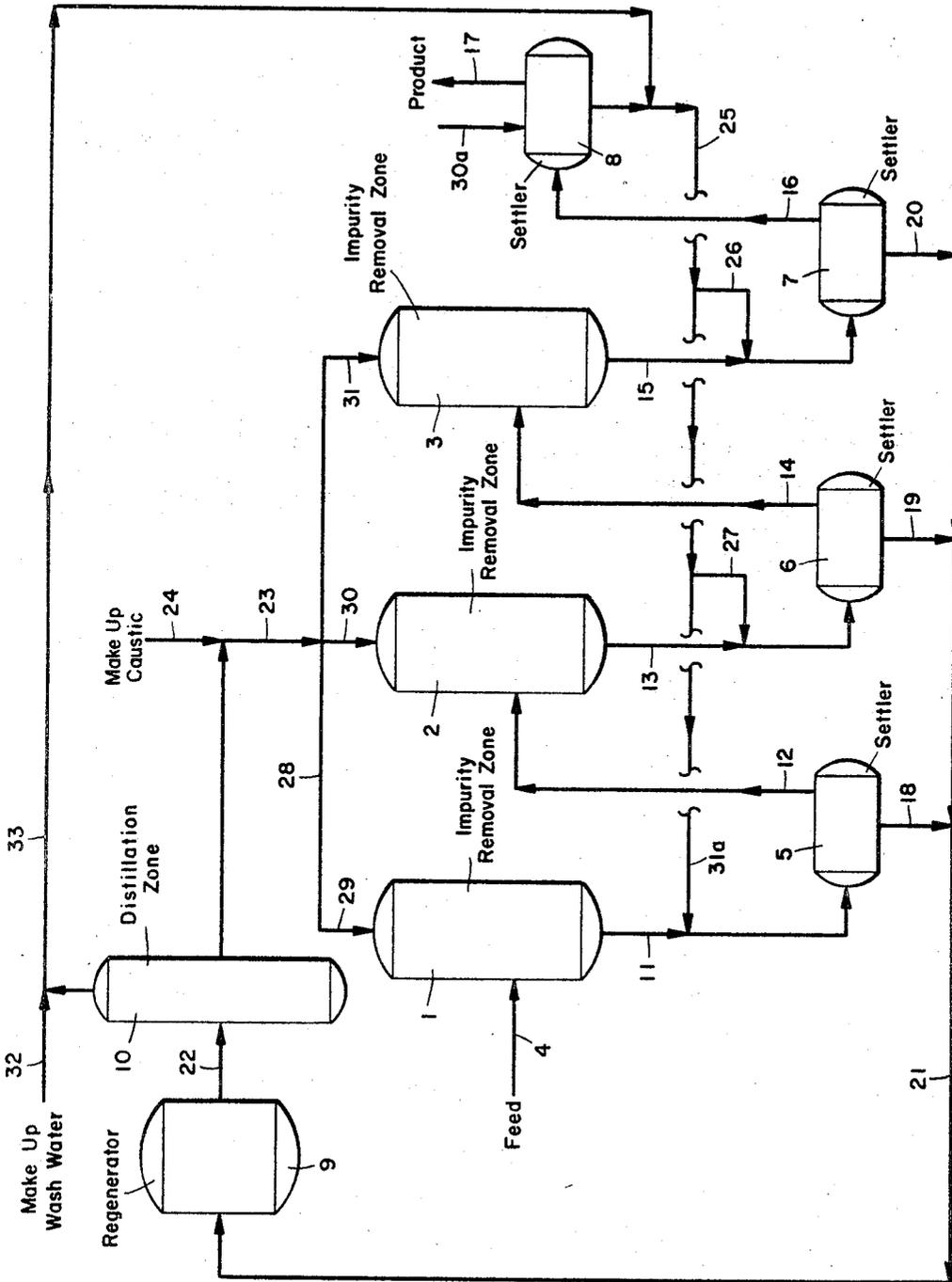


FIGURE 1

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FIGURE 2

DESULFURIZATION OF KUWAIT RESIDUUM

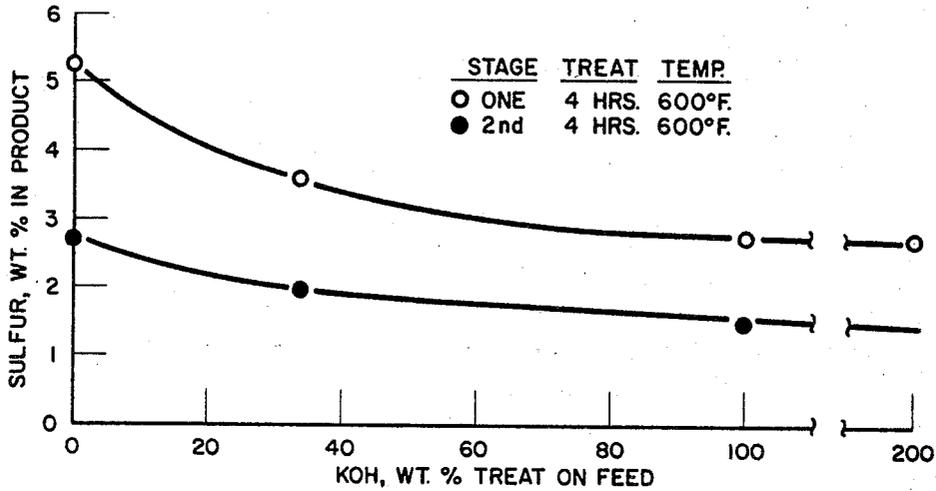
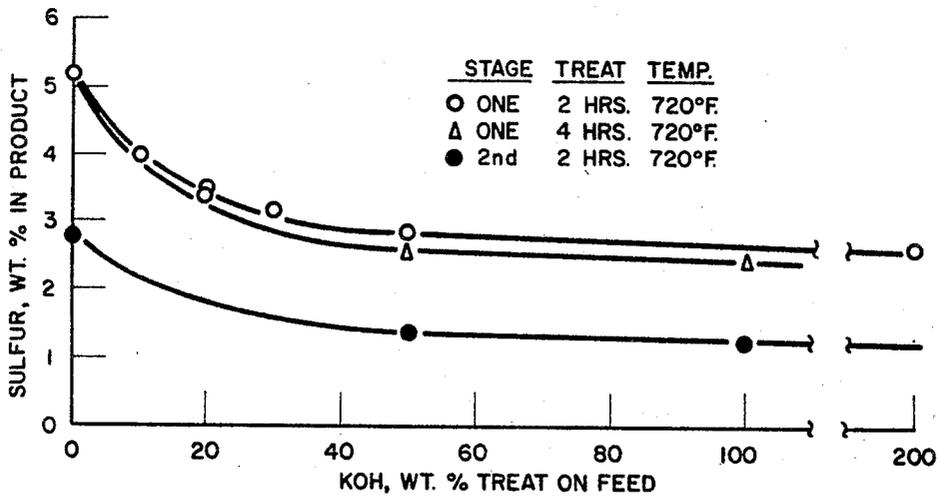


FIGURE 3

DESULFURIZATION OF KUWAIT RESIDUUM



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FIGURE 4
DESULFURIZATION OF KUWAIT RESIDUUM

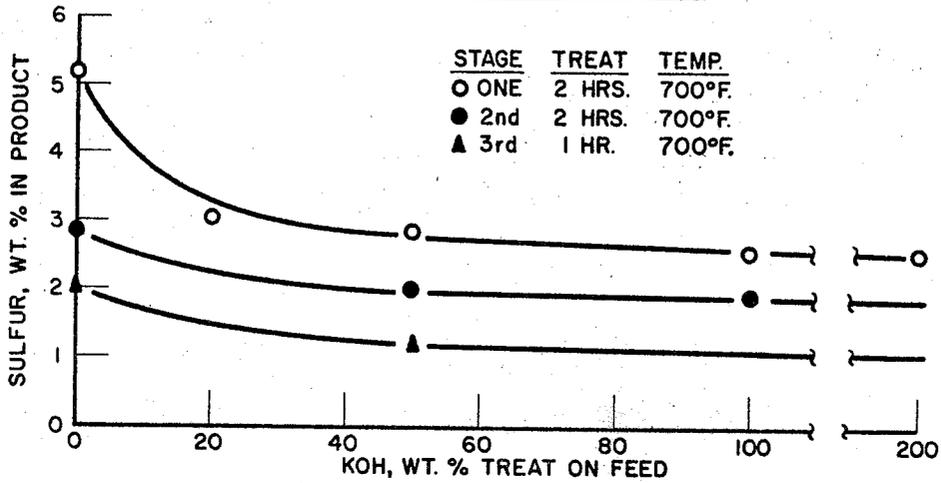
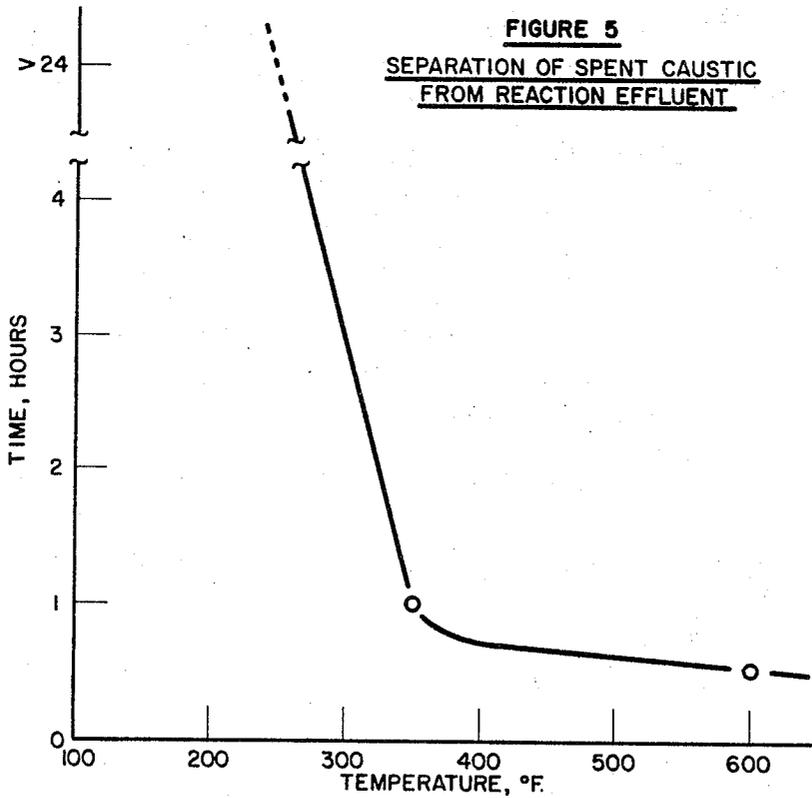


FIGURE 5
SEPARATION OF SPENT CAUSTIC FROM REACTION EFFLUENT



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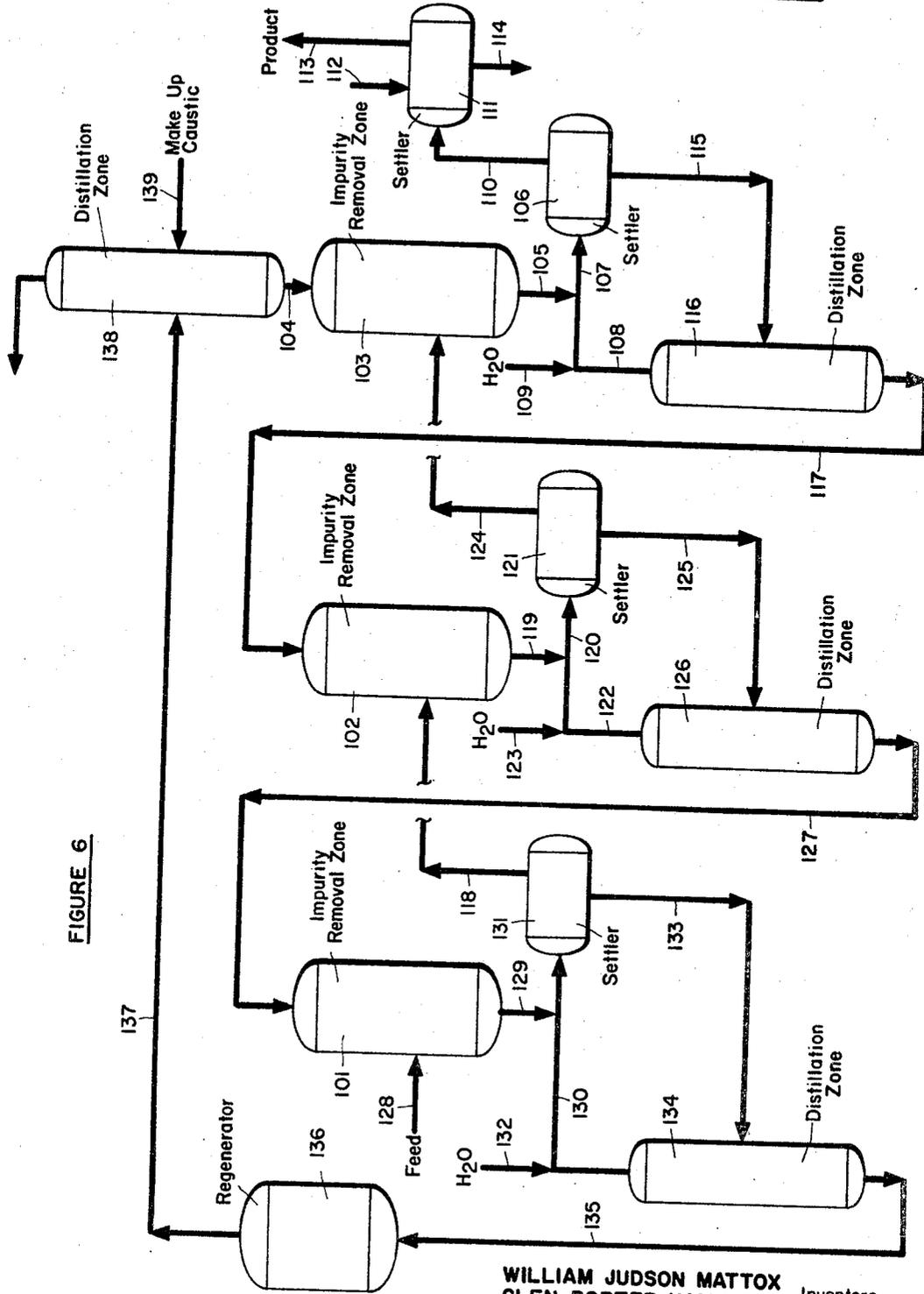


FIGURE 6

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DESULFURIZATION PROCESS FOR HEAVY PETROLEUM FRACTIONS

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 Continuation-in-part of application Ser. No. 290,522, June 25, 1963. This application Mar. 15, 1966, Ser. No. 547,102

U.S. Cl. 208—227 Int. Cl. C10g 19/02

5 Claims

ABSTRACT OF THE DISCLOSURE

This disclosure relates to the desulfurization of heavy petroleum fractions by means of an integrated process which includes at least two stages of contacting with a molten alkali metal hydroxide desulfurization agent.

The present invention concerns an improved process for removing sulfur, nitrogenous and metallic contaminants from petroleum fractions, such as fuel oil shale oil, residua, reduced or whole crudes. More particularly, the present invention relates to the use of molten alkali metal hydroxide containing from 5 to 30 wt. percent water, based on total reagent, to remove from heavy petroleum fractions the sulfur, nitrogenous, and metallic contaminants contained therein. Specifically, the invention relates to more efficient removal of impurities from the hydrocarbon fraction by staging of the feed and by staging of both the feed and molten alkali metal hydroxide reagent undergoing reaction. This application is continuation-in-part of our application Ser. No. 290,522, filed June 25, 1963, now abandoned.

Generally, sulfur occurs in petroleum stocks in one of the following forms: mercaptans, sulfides, disulfides, and as part of a substituted ring, of which thiophene is the prototype. The mercaptans are generally found in the lower boiling fractions, e.g., the naphtha, kerosene, and light gas oil. Numerous processes for sulfur removal from these lower boiling fractions have been suggested, such as "doctor" sweetening (wherein mercaptans are converted to disulfides), caustic treating, solvent extraction, copper chloride treating, etc., all of which give a more or less satisfactory decrease in sulfur or inactivation of mercaptans by their conversion into disulfides. When the process results in the latter effect, the disulfides generally remain in the treated product and must be removed by another step if it is desired to obtain a sulfur-free product.

Sulfur removal from higher boiling fractions, however, has been a much more difficult operation. Here the sulfur is present for the most part in the less reactive forms as sulfides, disulfides and as a part of a ring compound, such as a thiophene. Such sulfur is, of course, not susceptible to chemical operations satisfactory for removal of mercaptans. Extraction processes employing sulfur-selective solvents are also unsatisfactory because the high boiling petroleum fractions contain such a high percentage of sulfur-containing molecules. For example, even if a residuum contains only about 3% sulfur, it is estimated that substantially all of the molecules may contain sulfur. Thus, if such a residuum were extracted with a solvent selective to sulfur compounds, the bulk of the residuum would be extracted and lost.

Metallic contaminants, such as nickel and vanadium compounds, are found as innate constituents in practically all crude oils. These contaminants present another problem. Upon fractionation of the crudes, the metallic contaminants are concentrated in the residua which normally have initial boiling points of about 1000° F. Such residua

are conventionally used as heavy fuels, and it has been found that the metal contaminants there in adversely affect the combustion equipment in which the residua are burned. The contaminants not only form ash, which leads to sludging and the formation of deposits upon boiler tubes, combustion chamber walls, and gas turbine blades, but also attack the refractories which are used to line boilers and combustion chamber and severely corrode boiler tubes and other metallic surfaces with which they come into contact at high temperatures.

In the past, methods to chemically remove the sulfur have been ineffective to remove large amounts of sulfur and, furthermore, had little or no effect on the nitrogenous or metallic impurities, these materials requiring other methods for their removal.

It has been disclosed in U.S. Patent 3,164,545 that sulfur compounds and other impurities could be efficiently removed from various crude oils and hydrocarbon fractions by contacting the sulfur or impurity-containing fraction with molten alkali metal hydroxide. It was found, however, that the amount of sulfur that could be removed was limited. That is, the amount of sulfur that could effectively be removed from a particular fraction was limited. Increasing the amount of alkali metal hydroxide contacted with the particular sulfur-containing fraction above about 100 wt. percent did not result in any substantial increase in sulfur removal. To a certain extent, however, the concentration of alkali metal reagent contacted with the feed and the time of contact do have an effect on the amount of sulfur removal.

Temperatures within specified ranges were also found to have an effect, that is, increasing the temperature generally increased the amount of sulfur removed. Also, the holding time, or the time the sulfur-containing fraction was in contact with the molten alkali metal reagent, was significant up to about 4 to 6 hours; above about 4 to 6 hours, the amount of sulfur removal did not appreciably increase.

Though sulfur removal in a single stage treatment was relatively effective, and the percentage of sulfur removed varied somewhat with the particular crude fraction being treated, it was found that the molten alkali metal reagent, no matter how much was used, under the extreme conditions with prolonged holding time, was limited to removing a maximum of about 65% of the sulfur present in a particular oil being treated. This was true in spite of the use of large excesses of alkali metal reagent and the use of elevated temperatures and the extended periods of contact.

This technique of removing sulfur and other contaminants from contaminant-containing fractions, though effective, generally did not make for efficient utilization of the alkali metal hydroxide reagent, and good sulfur removal required relatively long treating periods.

It has now been discovered that contaminants can be removed by contacting the petroleum fraction with molten alkali metal hydroxide containing from about 5 wt. percent to about 30 wt. percent water, based on total reagent, under temperature conditions within the range of about 400° F. to 800° F. by carrying out the reaction in two or more stages.

Previously, it was considered that the limitations in sulfur removal with molten KOH was due to the character or the structure of the particular hydrocarbons containing the sulfur. That is, when oil containing a particular type or types of compound had reacted with molten KOH to liberate the sulfur from that type of compound, no more of the sulfur-containing compounds in that feed could be made to react to remove any more sulfur. This view was supported by the fact that as the ratio of, e.g., molten, KOH to feed increased, the curve representing

sulfur removal flattened out indicating that all such compounds that could had reacted with the KOH.

Also, since adding excessive amounts of the alkali reagent above the stoichiometric amount did not appreciably increase the desulfurization reaction, it was believed that the reaction was not equilibrium-limited.

Applicants unexpectedly found that a substantial further increase in sulfur removal could be achieved by taking the same total dosage for the same period of contact and carrying out the desulfurization in two or more stages for shorter contact periods and thereby substantially increase the total sulfur removal with the same total amount of KOH and the same total period of contact. For example, it was possible to remove as much as 75% of the sulfur in Kuwait vacuum residuum using two batch treatments with 50% KOH on oil per treat of 1 hour each whereas a single treat with 100% KOH on oil at two hours only reduced the sulfur content at about 52%. Applicants also found that there is a competing reaction in KOH desulfurization whereby K_2CO_3 is formed along with K_2S . The K_2CO_3 does not assist in the desulfurization reaction. The formation of K_2CO_3 can substantially increase the amount of KOH needed to carry out the desulfurization reaction.

At temperatures up to about 725 to 750° F., good desulfurization can be obtained. However, at temperatures above about 750° F., with some feeds the caustic is inefficiently utilized and converted preferentially to K_2CO_3 rather than K_2S .

Applicants found that the above limitations in sulfur removal can be overcome and more efficient utilization of KOH obtained by carrying out the contacting of KOH and feed in more than one stage. The application of staging is not novel, of course, in solvent extractions; however, the increase in utilization of KOH and the increase in sulfur removal with molten alkali metal hydroxide obtained by staging is completely unexpected. Applicants also unexpectedly found that in the subsequent stages the same degree of desulfurization can be obtained at lower severity of treatment or temperature and/or time as in the previous stage, with the result of a substantial decrease of gas make. Carrying out of the subsequent stages at lower temperatures and treating times also results in a substantial minimization of product degradation.

In order to obtain good contact between the alkali metal caustic reagent and the hydrocarbon being treated to remove the contaminants, it is necessary to thoroughly mix the reactants which frequently results in the formation of an emulsion. The emulsion was found very difficult to separate so that even if good desulfurization and other contaminant removal was obtained, the difficulty in separating the emulsion into a partially spent reagent layer and a desulfurized oil layer rendered the process inefficient. Applicants found that an efficient separation of the inorganic and oil products could be obtained by water-washing the product mixture at temperatures above about 350° F. with about 50 to 200 volume percent of water. One wash at above about 350° F., for example, with about an equal amount of water, based on molten alkali metal reagent, was found to be sufficient to remove almost all of the inorganic material as a clear aqueous solution which could easily be separated from the desulfurized oil layer.

Depending on the temperature of treatment during the desulfurization reaction and the particular feed treated, it may be desirable to add a light diluent to the reaction product mixture in order to decrease the viscosity of the oil prior to the water-wash step to aid in obtaining a good separation of oil and inorganic material. With some feeds it is desirable to carry out the water-wash step at temperatures as high as 600 to 700° F. in order to decompose organic carboxylic acid salts which may be formed during the desulfurization reaction. These organic acid salts contribute to the emulsion formation.

A clay filtration step may be utilized to remove any residual amounts of caustic in the desulfurized oil to less than 5 p.p.m. caustic.

FIGURE 1 is a diagrammatic representation of an embodiment of the invention wherein the sulfur-containing oil is contacted with molten alkali metal hydroxide in three stages and the spent molten hydroxide is subsequently regenerated and heated to remove excess water and recycled.

FIGURES 2, 3 and 4 are graphic illustrations showing the effectiveness of multi-stage treatment of a hydrocarbon fraction to remove sulfur. These graphic illustrations also show sulfur removal as a function of weight ratio of KOH on feed at various treating temperatures.

FIGURE 5 of the drawings shows the critical effect of temperature on settling and separation of the inorganic alkali metal caustic reagent from the desulfurized oil fraction.

FIGURE 6 is a diagrammatic representation of a three-stage process in which the feed flows through the units countercurrent to the flow of the treating agent.

By carrying out the invention in accordance with applicants' process whereby the feed is staged in two or more stages and/or the reagent is staged in two or more stages, a substantial increase in the utilization of the alkali metal reagent and a substantial increase in the amount of sulfur that can be removed is obtained. Being able to better utilize the caustic reagent substantially reduces the alkali metal reagent inventory that is required to carry out a specific amount of desulfurization of a particular feed; also, it greatly limits the requirements for pumps, distillation capacity to remove excess water from the separated alkali metal reagents, and regeneration capacity to regenerate alkali metal reagents. All these advantages result in considerable savings in investment in apparatus, reagent, and in processing costs.

Referring to FIGURE 1, a feed such as 950° F. Kuwait residuum is obtained from a suitable source and directed via line 4 to impurity removal zone 1, where it is contacted with molten alkali metal hydroxide containing 5 to 30 wt. percent water based on total reagent entering through line 29. The residuum and molten alkali metal hydroxide are intimately mixed which causes the sulfur, metallic and nitrogenous impurities in the residuum to react with the molten alkali metal hydroxide to form products which may be removed from the hydrocarbon oil with the partially spent reagent, thus yielding a high quality product. Although impurity removal zone 1 shown in the drawing is a batch step, it is to be understood that this process may be conducted continuously.

The amount of water in the molten alkali metal hydroxide is important for the improved results of the instant invention. The water content should be within the range of about 5 to 30 wt. percent based on total reagent, preferably 7 to 25 wt. percent, and more preferably 10 to 20 wt. percent. The most preferred water content is about 15 wt. percent, based on molten alkali metal hydroxide or $KOH \cdot \frac{1}{2}H_2O$. Temperature conditions during the contacting step should be maintained within the range of 400 to 800° F., preferably 450 to 750° F., more preferably 500 to 700° F. The amount of molten alkali metal hydroxide reagent (including water) used in each stage may be within the range of 10 to 200 wt. percent of the feed being treated, more generally 25 to 100 wt. percent, preferably 25 to 50 wt. percent. It is to be understood that depending on the amount of sulfur present and the amount of reagent used, the reagent is suitable for use in treating additional oil before regeneration is required. Usually, these ratios will represent an excess of reagent over that actually reacted with the sulfur so that at least a portion of the reagent separated from the treated oil could be recycled directly to a treating zone. Treating time may be as little as $\frac{1}{40}$ hour to 16 hours, generally the longer the time of contact, the greater the impurity removal. Generally, treating times

within the range of ½ to 6 hours are used. The preferred treating time per stage will be ½ to about 2 hours. The pressure may vary from 0 to 500 p.s.i.g., depending on the hydrocarbon feedstock, and is not critical to the desulfurization reaction.

The mixture of alkali metal hydroxide and hydrocarbon material leaves the impurity removal zone 1 through line 11 and is mixed with about 0.25 to 2.0 volumes of water/ volume of reaction mixture introduced through lines 25 and 31a, and passes to settling zone 5 at a temperature after mixing of above about 350° F. The water separates as a distinct phase from the treated residuum phase. The water layer will contain the reaction products of the impurities and the molten alkali metal hydroxide.

The molten alkali metal hydroxide phase recovered from settling zone 5 is directed via lines 18 and 21 to regeneration zone 9 for recycle. The partially desulfurized oil is removed from settler 5, taken overhead by line 12, and introduced into the second stage of the reaction, zone 2, wherein it is intimately mixed with fresh or regenerated caustic introduced through line 30. After a suitable treating time, it is removed through line 13 and introduced into settler 6. Prior to introduction to settler 6, it is mixed with about an equal portion of water and cooled to a temperature above about 350° F. In settler 6 the mixture quickly settles into an aqueous-free oil layer and an aqueous layer containing the inorganic contaminants. The aqueous layer containing alkali metal hydroxide and the removed inorganic contaminants are withdrawn through line 19. The oil, reduced again in sulfur content by about 50% of the sulfur content introduced into stage 2, is withdrawn overhead through line 14 and introduced into the third stage of the reaction in zone 3. In zone 3 it is mixed with fresh or regenerated caustic introduced through line 31 and allowed to react for a suitable length of time. The reaction products are withdrawn through line 15 and mixed with wash water introduced through line 26 and fed into settler 7 wherein it again separates into an aqueous inorganic layer and an aqueous-free oil layer. The aqueous-free oil layer is withdrawn overhead through line 16 and introduced into settler 8 wherein it is water-washed by water introduced through line 30a to remove any small amount of remaining caustic. The desulfurized oil, reduced by about 75% or more of its sulfur content, is withdrawn overhead through line 17 and taken to storage. The aqueous layer is withdrawn from settler 8 and is suitably mixed with recycle wash-water from line 33 and through line 25 supplies the wash-water to settlers 5, 6 and 7 through lines 25, 31a, 27 and 26. The inorganic aqueous layers from settlers 5, 6 and 7 are withdrawn through lines 18, 19 and 20 and combined in header 21 and are returned to regeneration zone 9 wherein the spent and/or partially spent molten alkali metal hydroxide is regenerated in regeneration zone 9 by suitable regeneration means, for example, those means shown in application Ser. No. 45,309, now U.S. Patent 3,128,155 and/or U.S. Patent 3,164,545, or other means. The regenerated caustic solution is withdrawn through line 22 and distilled in distillation zone 10 to remove, overhead, all the wash water introduced in the various settling operations, and reconcentrated so that the molten alkali metal treating reagent has a water concentration of between about 5 and 30% water. Depending on the means of regeneration, the excess wash water can be removed first. Make-up caustic can be added through line 24. The regenerated caustic, reconcentrated by removal of water, and make-up caustic are then introduced into reactors 1, 2 or 3 via lines 23, 28, and lines 29, 30, and 31. The water distilled from distillation zone 10 goes overhead through line 33 and make-up water can be added through line 32, as needed, and is fed to line 25 to supply the wash-water in each of settlers 5, 6 and 7.

Settling zones 5, 6, and 7 are maintained at a temperature above about 350° F. up to the temperatures in impurity removal zones 1, 2, and 3 in order to facilitate

gravity separation of oil and reagent and prevent heat loss from the caustic feed to regeneration zone 9.

Various conventional pieces of equipment which are used with embodiment of the invention shown in FIGURE 1, such as pumps, heat exchange apparatus, furnaces, and contacting devices, etc., have been omitted in order to simplify the drawing. The omitted equipment would be used in a manner known in the art and does not constitute part of the invention and, for these reasons, were not put in the drawing.

The dosage rate of fresh and/or regenerated caustic to each stage can be varied until the optimum rate of KOH utilization for each subsequent stage is determined or each can be maintained at the same rate as fed to the first stage since any excess unreacted KOH from the subsequent stages which does not react to remove sulfur is merely recycled and regenerated. However, determining the optimum dosage rates would be an advantage since it would decrease the load on each of the settlers and on the distillation tower since the amount of water required to obtain a good separation under specific settling conditions increases with the dosage rate of caustic contacted with the feed to be desulfurized. The entire process may be carried out as a continuous or batch process.

FIGURE 1 is a scheme for effective feed staging under fresh reagent in each stage. However, both feed staging and reagent staging can be obtained in an apparatus similar to that in FIGURE 1 by making several process variations.

For example, referring to FIGURE 6, all the fresh reagent can be fed by line 104 to the last stage, zone 103, of the reactors and contacted with feed which is already substantially reduced in sulfur content by virtue of previous stages of treatment in zones 101 and 102. The reaction mixture from zone 103 is passed by lines 105 and 107 to settler 106. Water from line 108 and/or line 109 is added in approximately equal amounts and the mixture is allowed to settle. The desulfurized oil is removed by line 110 and passed to settler 111. The oil is washed with water added by line 112. Product oil is removed by line 113. Wash water containing a small amount of caustic is removed by line 114. The caustic may be recovered from this water if desired. Dilute, partially spent caustic is removed from settler 106 by line 115 and passed to distillation zone 116. Distillation is carried out at conditions suitable to concentrate the reagent at about 5-30 wt. percent water. Reconcentrated caustic is passed by line 117 to zone 102 where it is reacted with partially desulfurized oil entering the reactor from line 118. The reaction mixture from zone 102 is passed by lines 119 and 120 to settle 121. Water from line 122 and/or 123 is added in approximately equal amounts and the mixture is allowed to settle. The partially desulfurized oil is passed by line 124 to zone 103. Dilute, partially spent caustic is removed from settler 121 by line 125 and passed to distillation zone 126. Partially spent, reconcentrated caustic is passed by line 127 to zone 101 where it is reacted with fresh feed entering the reactor from line 128. The reaction mixture from zone 101 is passed by lines 129 and 130 to settler 131. Water from line 130 and/or line 132 is added in approximately equal amounts and the mixture is allowed to settle. Dilute, partially spent caustic is removed from settled 131 by line 133 and passed to distillation zone 134. Spent caustic is passed by line 135 to regenerator 136. The spent alkali metal hydroxide is regenerated by suitable regeneration means such as the means disclosed in U.S. Patent 3,164,545 or other means. The regenerated caustic is passed by line 137 to distillation zone 138. In this zone, makeup caustic is added by line 139 and the water content of the caustic is adjusted to a concentration of 5-30 wt. percent. The caustic is added to zone 103 by line 104 and another countercurrent contacting series is carried out. By countercurrent contacting we mean that the caustic flows from right to left through the processing units of FIGURE 6

and the feed flows from left to right intimately contacting the caustic moving in the opposite direction. Reaction and separating conditions for operations involving both feed staging and reagent staging are similar to those mentioned previously. However, the temperature and contacting time can be less in each of the reaction zones after contacting in the first zone.

This technique allows for feed staging as well as reagent staging. The fresh reagent is contacted with the feed having the lowest sulfur concentration and the most used and partially spent caustic is contacted with the feed having the highest sulfur content. This technique allows for a considerable amount of flexibility in caustic dosage rates, and for good overall utilization of caustic.

The following examples illustrate the various embodiments of the present invention.

Example 1

Batch tests were made on a 950° F. + Kuwait residuum containing 5.2 wt. percent sulfur with molten KOH containing water to determine the effect of varying the amount of KOH, the water content thereof, the temperature conditions and the treating time. The individual tests were conducted by adding the indicated amount of potassium hydroxide to the oil at 300 to 400° F. with stirring, increasing the temperature to the designated level and maintaining it there for the specified time with continuous high speed and mechanical stirring. After cooling to about 250–300° F., xylene or other comparable hydrocarbon was added to facilitate separation of oil from potassium hydroxide and the diluent removed from the treated product by distillation. In some instances where K₂S remained suspended in the oil, the sulfide was decomposed with acid preceding the removal of the xylene. The results are shown in Table I below:

TABLE I.—EFFECT OF OPERATING CONDITIONS ON DESULFURIZATION AND DEMETALIZATION WITH MOLTEN KOH-H₂O MIXTURE
One-Stage Operations

Wt. Percent H ₂ O in KOH-H ₂ O mixture	Wt. Percent KOH on feed	Temp., °F.	Treat, hours	Percent desulfurization	Percent V removed
Effect of Amount of KOH-H ₂ O Mixture					
15	34	600	4	31	-----
15	100	600	4	47	-----
15	200	600	4	46	-----
Effect of Water Content on Molten KOH					
2	100	600	4	10	-----
7	100	600	4	23	60
15	100	600	4	47	100
25	100	600	4	31	55
Effect of Temperature					
15	100	550	4	31	100
15	100	600	4	47	100
15	100	650	3.3	64	100
Effect of Treating Time					
15	100	600	1	28	-----
15	100	600	4	47	-----
15	100	600	16	60	-----

¹ These data also illustrate the water retentive characteristics of KOH at different temperatures as little or no water was lost from the molten reagent during treatment.

TABLE II.—METAL AND SULFUR REMOVAL WITH MOLTEN KOH-H₂O REAGENT¹
One-Stage Operation

Contacting vessel..... Feed.....	Nickel-lined autoclave		Open vessel				
	400° F.+Heavy Lake Mix	700° F.+Kuwait	950° F.+Kuwait	650° F.+Heavy Lake Mix			
Treating temp., ° F.....	650	700	600	600			
Contact time, hrs.....	2.5	4.0	4.0	2			
Inspections	Feed	Product	Feed	Product	Feed	Product	
Vanadium, p.p.m.....	400	20	40	5	90	5	700
Percent removed.....		95		88		95	100
Sulfur, wt. percent.....	2.5	2.0	4.2	2.9	5.2	2.8	
Percent removed.....		20		31		46	
Nickel, p.p.m.....						100	
Percent removed.....							0.5
							100

¹ These data also illustrated the water retentive characteristics of KOH at atmospheric pressures and elevated temperatures as little or no water was lost from the molten reagent during treatment either from the autoclave or open vessel tests.

From the above table it is clear that these variables all affect the desulfurization of the residuum. The effect on sulfur removal with molten KOH reagent within the range of 25 to 200 wt. percent of feed being treated, preferably 50 to 150 wt. percent is shown. The water content of the molten KOH should be within the range of 5 to 30 wt. percent, preferably 7 to 25 wt. percent. The optimum water content would be about 15 wt. percent water. As is seen above, the temperature substantially affects the desulfurization obtained and the temperature during contacting should be in the range of about 400 to 800° F., preferably 450 to 750° F., and more preferably 500 to 700° F. Furthermore, the longer the treating time the more the desulfurization, but with increased treating times greater than about 4 to 6 hours the relative effectiveness decreases. It is preferred that treating times within the range of about ¼ to 4 hours be employed.

The above data were obtained from one-stage operations. The conditions given for the one-stage operations are generally applicable to the two- and three- or more stage operations. This is modified to the extent that it was unexpectedly found that subsequent stage operations could be carried out at lower severities of temperature and time and still obtain good desulfurization, yet minimizing the degradation of the product due to gas yield. Generally, though, the above amount of alkali metal reagent based on feed contacted with the oil being treated could be within the broad ranges discussed above. It is generally preferable, for purposes of better utilization of reagent, however, to contact the oil being treated with, for example, 20–50 wt. percent reagent in each of the two or more stages with each of the stages reduced in treating time so that the overall treating time and the overall reagent used would be approximately the same for the maximum efficient desulfurization as carried out in a single stage.

Example 2

This experiment was conducted to demonstrate the high removal of sulfur and metals which is obtained by use of the molten KOH containing water of the instant invention. The experiments were conducted in two physically different environments; namely, an autoclave and an open stainless steel vessel. Three different feeds were tested. In two runs the autoclave was used to avoid loss of light hydrocarbons from the more volatile feeds. Contacting and oil recovery in both the autoclave and open vessel tests were accomplished by the same general procedure as described in Example 1.

The results of the experiments are given in Table II below with the temperature and contact time of each run. In each test the molten KOH contained 15 wt. percent water based on total reagent and the reagent was present in equal amounts by weight to the feed being treated. Only traces of gas or coke were formed during these tests.

Example 3

In order to show comparatively the advantage obtained in two-stage treatment with molten alkali metal hydroxide as compared with the two- and three-stage treatment and to show the effect of temperatures varying between 600–720° F., the following runs were carried out. A Kuwait vacuum residuum having an API gravity of 6.2, Conradson carbon of 8.3 wt. percent, a sulfur content of 5.4 wt. percent, nitrogen 0.36 wt. percent, nickel 27 p.p.m., vanadium 70 p.p.m., and having an initial boiling point (atmospheric equivalent) of 847° F. and a final boiling point (atmospheric equivalent) of 1047° F. at 10% overhead was contacted with from 0 to 200 wt. percent of molten alkali metal caustic having 15% water in the molten alkali metal caustic for a period of 4 hours in each stage. The reaction was carried out at 600° F. in both the first and second stage. Desulfurization resulting from the contacting is shown graphically in FIGURE 2 of the drawings. It can be seen from this drawing that the maximum sulfur removal in the one-stage treatment obtainable even at 100% alkali metal caustic reagent is about 46 wt. percent. A second stage will reduce the amount of sulfur left again by about 40 to 50 wt. percent so that it is possible, for example, using two 50 wt. percent treatments of KOH, to remove substantially more sulfur than can be removed from a one-step 100% dosage treatment.

FIGURE 3 of the drawings illustrates a one-stage and two-stage contacting for removal of sulfur from the same residuum and under the same conditions except that the temperature is 720° F. It can readily be seen that increasing the temperature from about 600° F. to about 720° F. results in substantial increase in the amount of sulfur removed at each stage of the treatment.

FIGURE 4 of the drawings illustrates a three-stage treatment carried out at about 700° F.; otherwise, the same conditions as FIGURES 2 and 3. From FIGURE 4 it can be seen that at about a 50% dosage rate the sulfur present in the feed fed to a particular stage of reaction is reduced by about 40 to 50% of that amount of sulfur present, in each stage, and that providing excessive amounts of caustic does not appreciably increase the amount of sulfur removed. The conditions and the results obtained from the reactions illustrated in FIGURES 3 and 4 are shown below in Table III.

TABLE III

Stage.....	A			B		
	1	1	2	1	2	3
Temperature, ° F.	720	720	720	700	700	700
Wt. percent KOH on feed.....	100	50	50	50	50	50
Hours treat.....	4	2	2	2	2	1
Product Oil: wt. percent S.....	2.4	2.8	1.4	2.8	2.0	1.2
Percent desulfurization:						
On fresh feed.....	55	48	74	48	63	78
On feed to stage.....	55	48	50	48	29	40
Wt. percent gas formed.....	0.6	0.4	1.8	0.4	0.4	1.0
Spent KOH analysis, wt. percent:						
KOH.....				54	79	74
K ₂ S as KOH.....				18	7	12
K ₂ CO ₃ as KOH.....				28	14	14

It is noted that with two stages a greater degree of desulfurization is obtained than with one stage utilizing the same time and amount of KOH. For example, referring to column A, a 100% dosage treatment carried out for four hours produced a 55% desulfurization. By carrying out the desulfurization in two stages of 50% dosage for two hours in each stage, 74% desulfurization was obtained. The second and third stage, referring to column B, gives almost the same degree of desulfurization in each stage based on feed to the stage as was obtained in the first stage. Of particular interest is the amount of gas formed in the subsequent stages. In the subsequent stages, a higher amount of gas is formed so that it is desirable to reduce the severity of operation by reducing temperature and/or time of contact. In spite of this reduction in severity (i.e., time 1 hour versus 2 hours), it was found in stage 3 of

the 700° F. run that the degree of desulfurization was not materially decreased.

In staged treatment with KOH, in the last stage when sulfur was reduced from 5.4% to below 1.5 wt. percent, there was a significant increase in the amount of gas produced. It is considered likely that the cause of this increase in gas-make at this level of sulfur reduction is due to the reaction of certain types of sulfur compound which inherently produce more gas.

As noted by the analyses of the caustic recovered from the various stages there is considerable KOH remaining from the later stages which could be utilized for desulfurization in the initial stages. This staging of caustic as well as feed would allow greater utilization of the caustic. Use of this technique will allow good desulfurization of distillates and low sulfur feeds which have not usually been considered practical to treat by fused KOH in the past.

It would be expected that by using countercurrent flow of oil and caustic with multistaging of both components that improved utilization of the caustic as well as a high degree of sulfur removal would result. The caustic phase recovered from the second and third stage treats contain more than 75% free caustic. This caustic should be effective for desulfurization in the initial stage.

Example 4

Applicants found that the temperature at which the settling of the reaction mixture was carried out, from either the first, second, or third stages of the desulfurization reaction zones, was particularly critical in obtaining efficient settling. It was unexpectedly discovered that the reaction mixture could rapidly be settled at temperatures above about 350° F. To illustrate this, applicants contacted a Kuwait vacuum residuum of the type described in Example 3 at 700° F. for two hours with about 50 volume percent molten KOH reagent containing 15 wt. percent H₂O. Several samples from this reaction were separated and were mixed with about an equal portion of water and cooled to the temperatures indicated in the graph illustrated in FIGURE 5 of the drawings. It was found that at temperatures below about 350° F., the emulsion was stable or required an excessively long period of time to obtain an efficient separation of oil from inorganic aqueous solution. However, at about 350° F. and above, a sharp separation was found to occur in the reaction mixture, allowing an efficient separation of an aqueous-free desulfurized oil and an aqueous inorganic layer. The results obtained are shown below in Table IV.

Treat at 700° F. with KOH for 2 hours with 15% H₂O in KOH

Wash temp., ° F.	Separation after 1 hour
750	Good.
600	Good.
500	Good.
400	Good.
350	Satisfactory.
300	Fair.
200	Poor.
100	None.

The separation of the inorganic products from the product oil in KOH desulfurization of petroleum residuums and heavy crudes has been difficult to accomplish in the past. Such a separation, however, is necessary in order to take advantage of the sulfur removal possible with molten alkali metal reagents. In a commercial process it will be necessary to recover all but trace amounts of the potassium compounds for regeneration to KOH for reuse and to remove all but trace amounts of potassium from the oil before use as a fuel.

Applicants found that the inorganic and oil phase from KOH desulfurization can be separated readily by a simple water-wash at temperatures above about 350° F. if the desulfurization step is carried out under conditions of time and temperature so that a viscosity reduction of the

oil phase is effected. It is necessary that this viscosity reduction is sufficient to reduce the viscosity of the product oil to less than 100 SSU at 350° F. and preferably less than 50 SSU at 350° F. Such desulfurization conditions will depend somewhat on the feed used and can be obtained at temperatures of about 650 to 750° F. with one hour contact time. There is an inverse relationship between time and temperature so that at higher temperatures less time is required.

The water-wash is effectively carried out by intimately contacting the product mixture with an equal weight of water on KOH at a temperature such that on cooling, the temperature of the mixture is above about 350° F. and allowing the phases to separate at this temperature by gravity settling. The product oil may be subsequently treated by filtration, centrifugation or clay treatment to separate trace amounts of residual water or residual caustic.

The critical nature of this sequence of viscosity reduction and high temperature settling is illustrated by results obtained with Kuwait vacuum residuum. Desulfurization of the residuum with 20% KOH on oil by contacting for one hour at 720° F. did not allow good separation of the water wash at 350° F. Contacting for 2 hours at 720° F. did result in good separation. This viscosity reduction effected is, of course, beneficial for subsequent use of the product oil, as such a viscosity reduction is usually required to produce a salable product.

The exact settling time and treating temperature as well as ratio of water to KOH in the emulsion will vary somewhat with the viscosity of a particular feed being treated.

We claim:

1. An improved process for removing sulfur from a hydrocarbon stream which contains sulfur which comprises countercurrently contacting a molten alkali metal hydroxide reagent with the hydrocarbon stream in at least three stages to remove sulfur from said stream, said molten alkali metal hydroxide reagent containing 5 to 30 wt. percent water, said contacting being carried out for a period of time of ¼ to about 4 hours in each stage, whereby the sulfur concentration in the feed fed to each stage is reduced by about 30 to 60 wt. percent of the sulfur in the feed fed to that stage; in the first stage reaction zone the hydrocarbon feed is contacted with partially spent molten alkali metal hydroxide reagent, reacted, and the reaction mixture withdrawn from the reactor and fed to a settler where it is contacted with water and the mixture allowed to separate into two phases, a hydrocarbon phase and an aqueous phase; the two phases are separated and the aqueous phase is sent to an alkali metal reagent regeneration system, regenerated and subsequently treated to distill overhead excess water, the regenerated alkali metal hydroxide reagent is fed to the third stage; the partially desulfurized oil from the first stage is then fed to a second stage reaction zone where it is contacted with partially spent alkali metal hydroxide reagent, reacted, removed, contacted with water, and fed to a settler where it is separated into two phases, a desulfurized oil phase and an aqueous phase, the aqueous phase is fed to a distillation zone where excess water is removed and the concentrated molten alkali hydroxide reagent is fed to the first stage; the desulfurized oil is removed from the settler and fed to a third stage reaction zone where it is contacted with substantially fresh molten alkali metal hydroxide reagent and reacted, the reaction mixture removed to a settler where it is washed with water and al-

lowed to separate into two layers, an aqueous layer and a hydrocarbon layer; the aqueous layer is fed to a distillation tower wherein the water is removed overhead and the concentrated, partially spent alkali metal hydroxide reagent is fed to the second stage reaction zone; the desulfurized oil, substantially reduced in sulfur concentration, is removed and fed to a wash zone where it is contacted with a suitable wash liquid to remove any entrained alkali metal hydroxide reagent, allowed to settle and removed and taken to storage.

2. The process of claim 1 wherein the contacting in each of the reaction zones is carried out at temperatures between about 400 and 800° F. and the dosage rate of reagent contacted with the hydrocarbon feed is about 10 to about 100 wt. percent based on feed.

3. The process of desulfurizing a petroleum hydrocarbon fraction containing constituents boiling above about 950° F., and which contains sulfur in the less reactive forms as sulfides, disulfides and thiophenes comprising the steps of:

(a) Contacting said fraction in a first stage with 10 to 100 wt. percent of a molten potassium hydroxide reagent containing 5 to 30% water for from ½ to 4 hours, whereby the sulfur content of the oil fed to said first stage is reduced from 30-60 wt. percent;

(b) Withdrawing the reaction products from the first stage reaction and contacting them in a separation zone with a suitable solvent whereby said products are separated into two distinct phases, an upper phase containing the partially desulfurized hydrocarbon oil and a lower phase containing an aqueous solution of the alkali metal reagent and some of the sulfur contaminants from the oil;

(c) Separating the partially desulfurized oil layer from the aqueous layer;

(d) Contacting the partially desulfurized oil in a second stage with 10 to 100 wt. percent of a molten potassium hydroxide reagent containing 5 to 30% water for from ½ to 4 hours, whereby the sulfur content of the oil fed to said second stage is reduced from 30-60 wt. percent;

(e) withdrawing the reaction products from the second stage reaction and contacting them in a separation zone with a suitable solvent, whereby said products are separated into two distinct phases, a desulfurized oil phase and an aqueous phase containing the partially spent potassium hydroxide reagent; and

(f) Recovering the desulfurized oil phase.

4. The process of claim 3 wherein the temperature and period of contact is less in each of the reaction zones after the first zone.

5. The process of claim 3 wherein the process is carried out as a continuous countercurrent process.

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