

[54] **ALKALI METAL DESULFURIZATION
PROCESS FOR PETROLEUM OIL STOCKS
USING LOW PRESSURE HYDROGEN**

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208/294, 208/235, 204/68

[51] Int. Cl. C10g 19/00, C10g 17/00

[58] Field of Search 208/208 M, 230, 229, 294, 235,
208/209, 210; 204/68

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[57] **ABSTRACT**

Low sulfur-content petroleum oil stocks are prepared by contacting a sulfur-containing oil stock with an alkali metal, preferably sodium, or an alkali metal alloy, preferably sodium/lead, thereby producing a mixture comprising a low sulfur content oil containing alkali metal salts dispersed therein. The alkali metal treating step is conducted in the presence of low pressure hydrogen, i.e., 25 to 500 psig. The resulting mixture is then treated with either water or H₂S thereby disengaging a substantial portion of the salts from the oil. The salt phase is then blended with a molten sulfur-rich alkali metal polysulfide thereby forming a sulfur-depleted alkali metal polysulfide which is subsequently decomposed electrolytically to form alkali metal.

19 Claims, 6 Drawing Figures

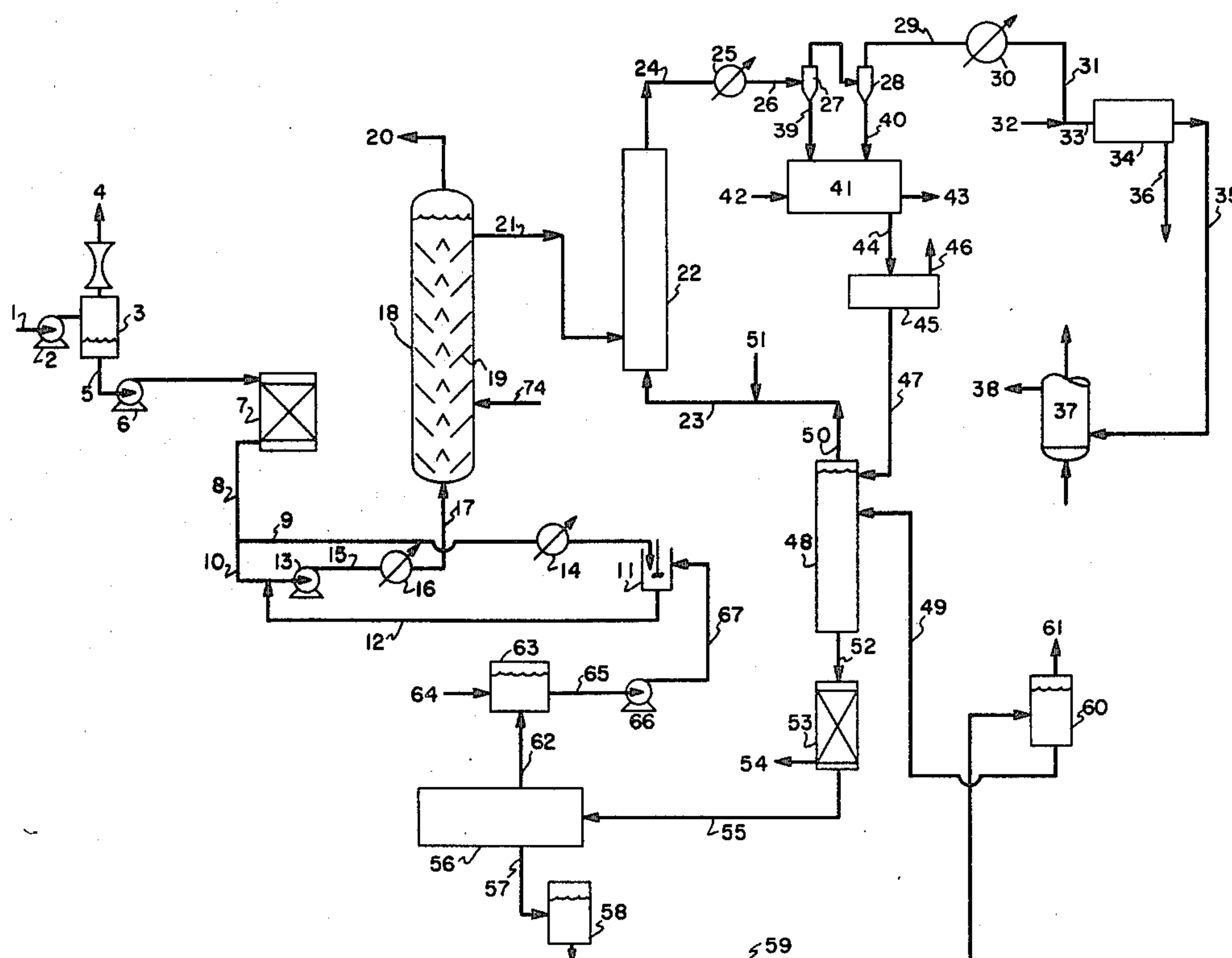


FIGURE 1

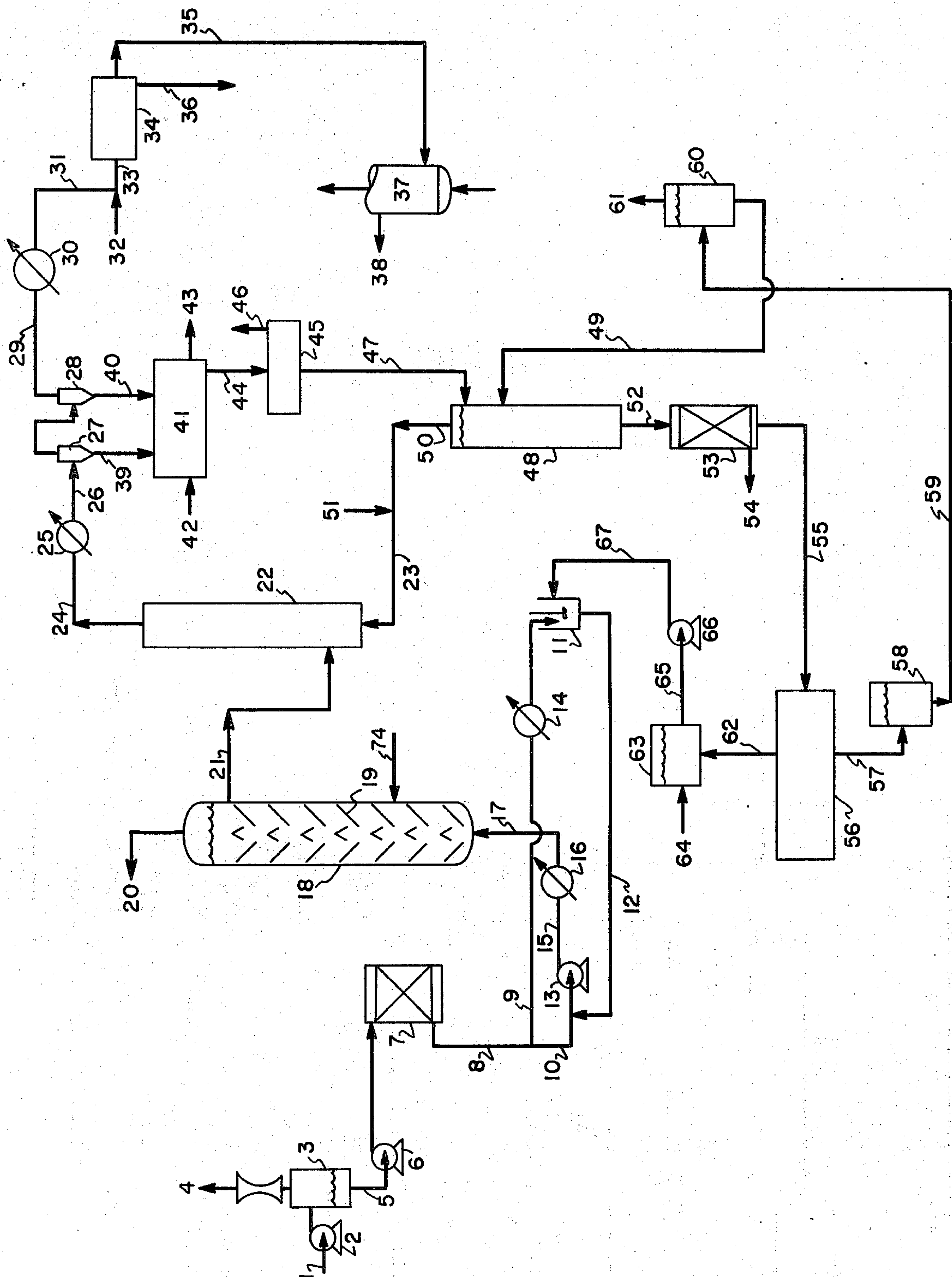


FIGURE 2

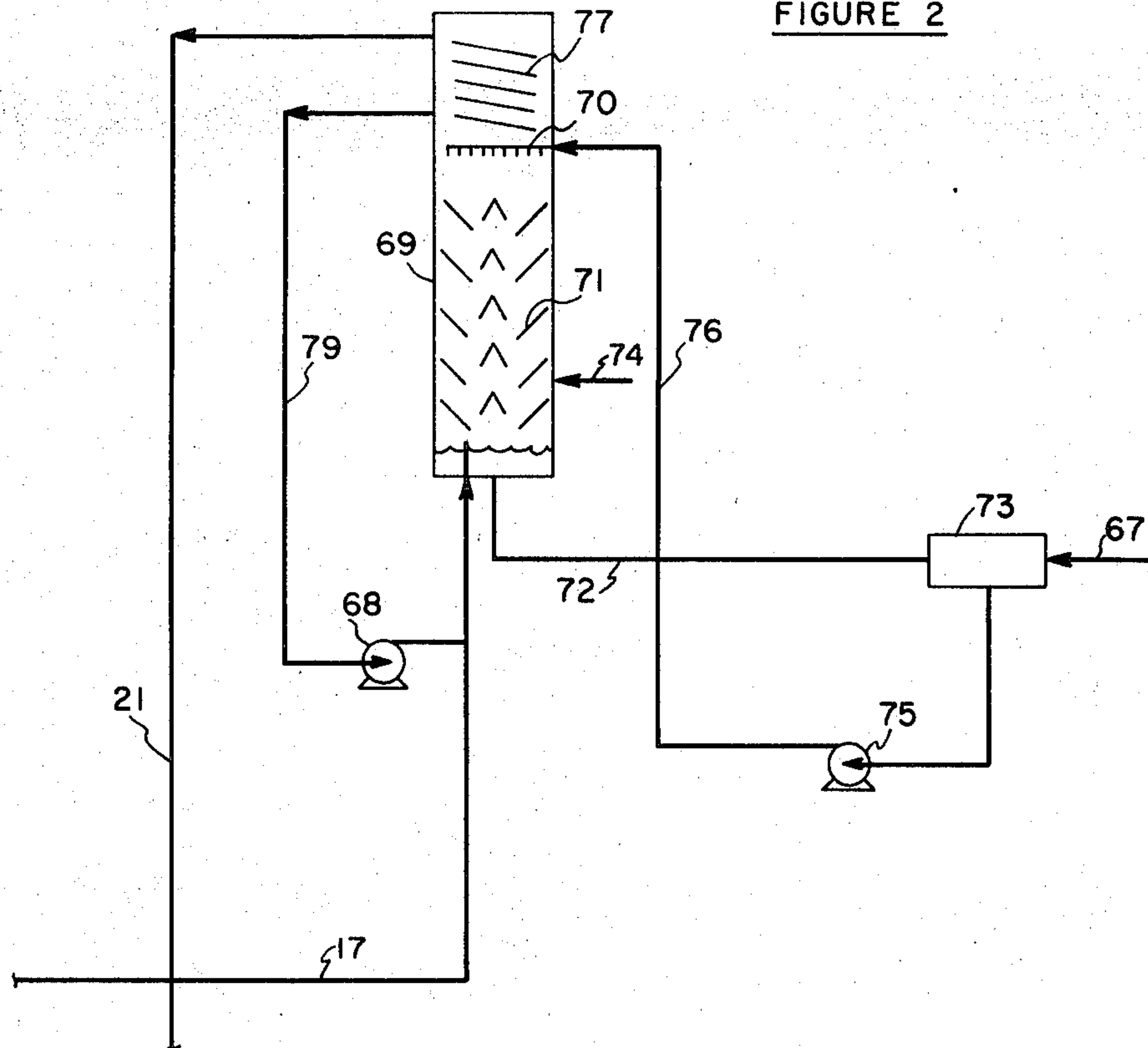


FIGURE 3

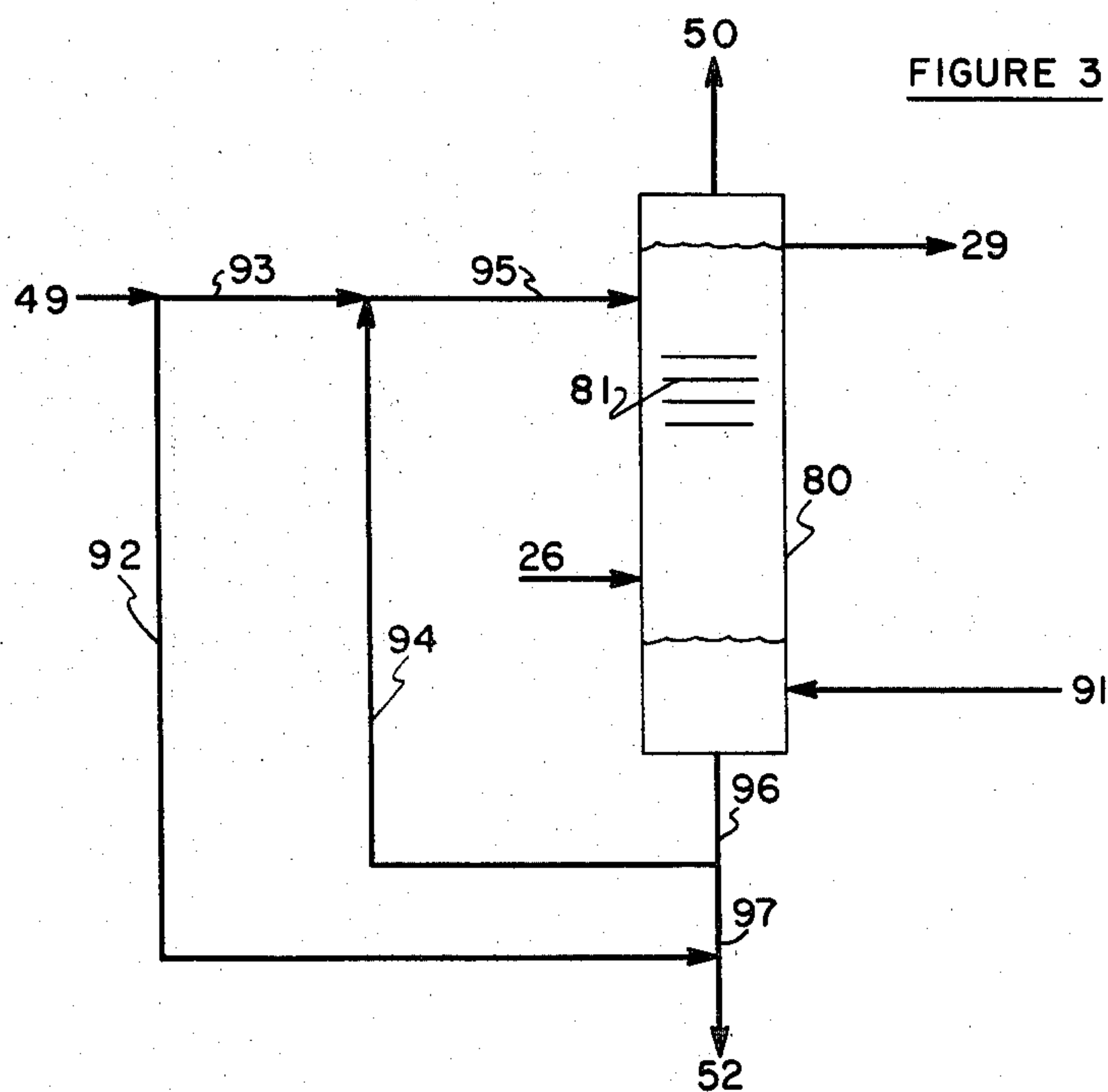


FIGURE 4

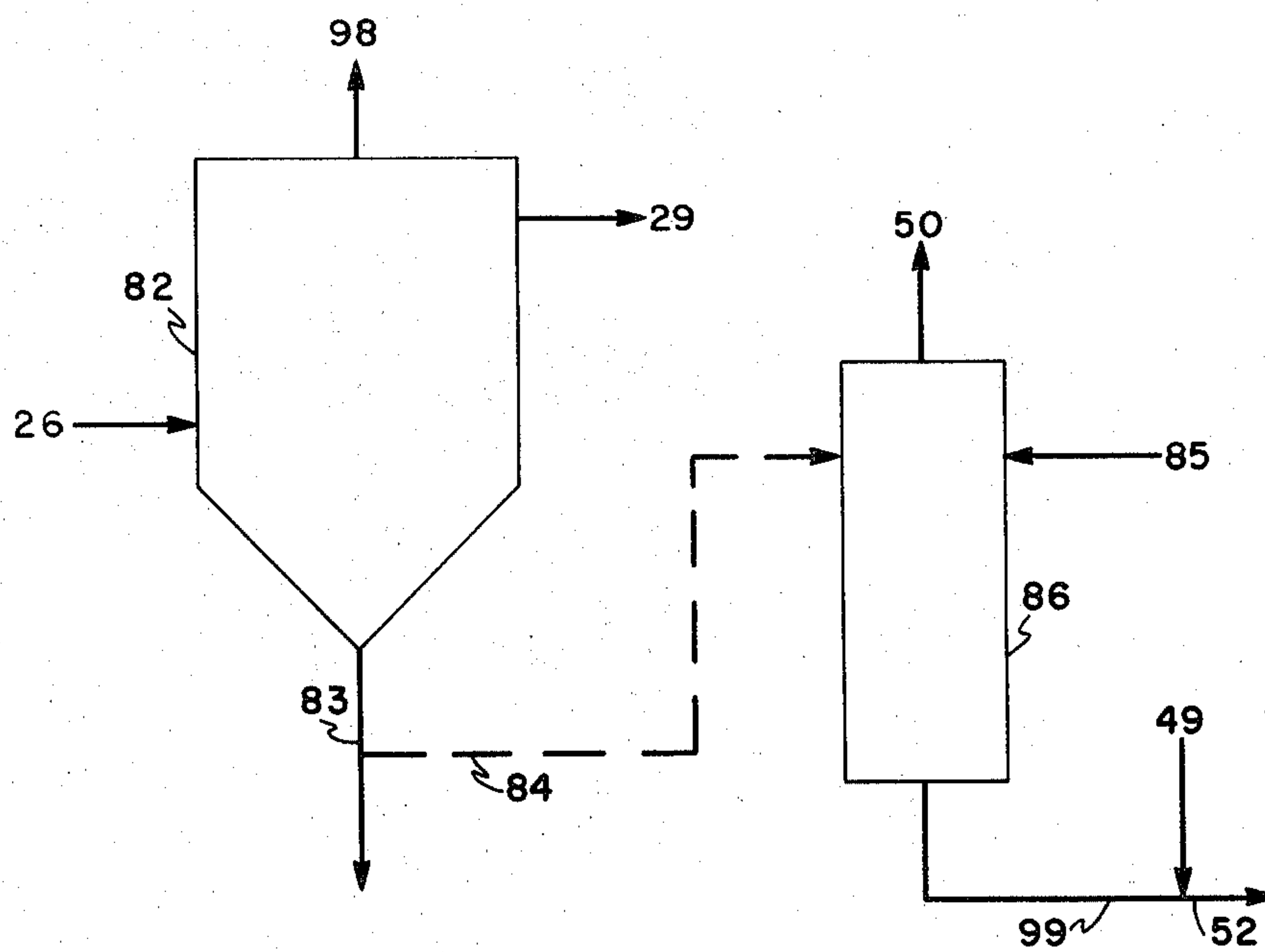
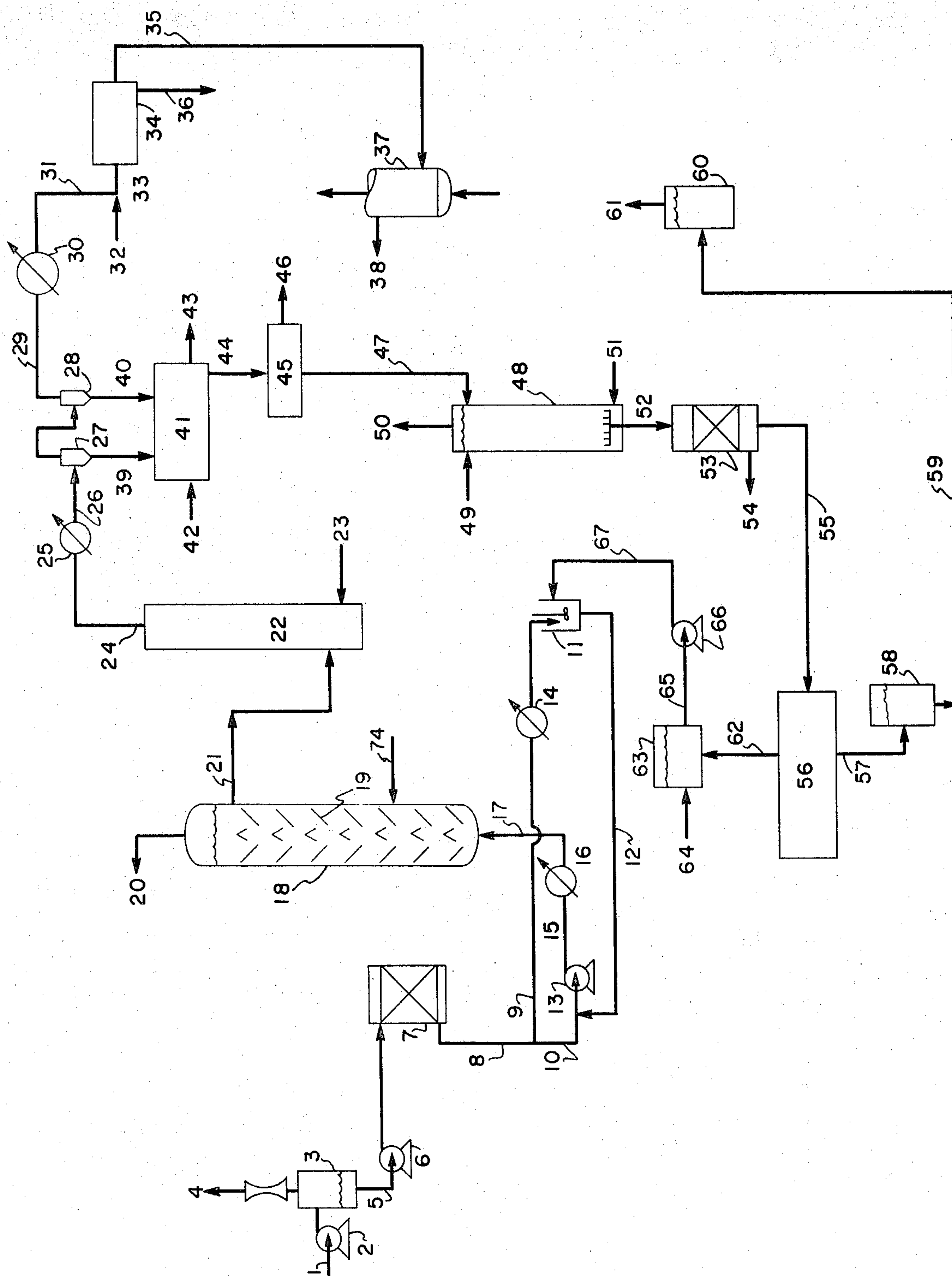


FIGURE 5



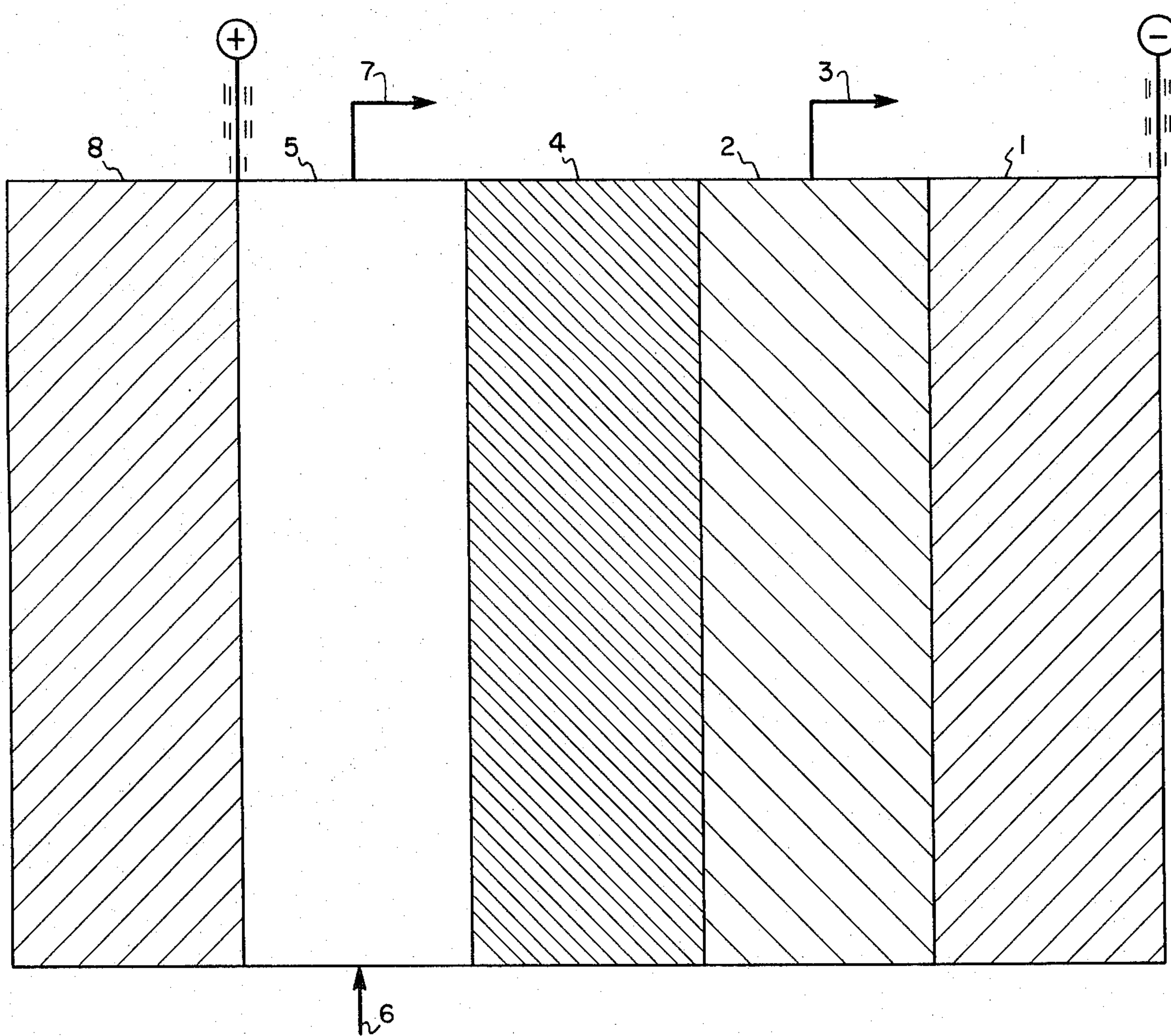


FIGURE 6

ALKALI METAL DESULFURIZATION PROCESS FOR PETROLEUM OIL STOCKS USING LOW PRESSURE HYDROGEN

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for the desulfurization of sulfur-containing petroleum oil stocks. More particularly, the process comprises contacting a sulfur-containing oil stock with an alkali metal or alkali metal alloy.

2. Description of the Prior Art

In the last several years there has been an ever-increasing concern about air pollution. Some of the objects of this concern have been the discharge of sulfur oxides to the atmosphere upon burning sulfur-containing fuels. Over a period of many years several studies have been conducted with the object of developing efficient and economical means for reducing the sulfur content of crude petroleum oils and other virgin hydrocarbon fractions.

To the present, the most practical desulfurization process has been hydrogenation of sulfur-containing oils at elevated pressures and temperatures in the presence of an appropriate catalyst. The process requires the use of hydrogen pressures ranging preferably from about 700 to about 2,500 psig and temperatures ranging from about 650° to about 800°F., depending on the nature of the oil to be desulfurized and the amount of sulfur required to be removed.

The process is efficient in the case of distillate oil feedstocks but less efficient when used with those containing undistilled oil such as whole crudes or residua. This is due to several factors. First, most of the sulfur in the oils is contained in high molecular weight molecules, and it is difficult for them to diffuse through the catalyst pores to the catalyst surface. Furthermore, once at the surface, it is difficult for the sulfur atoms contained in the molecules to "see" the catalyst surface. Additionally, the feedstocks may contain large amounts of asphaltenes which tend to form coke deposits under the process conditions on the catalyst surface thereby deactivating the catalyst. Moreover, high boiling organometallic compounds present in such oil stocks decompose and deposit metals on the catalyst surface thereby diminishing the catalyst life time. The severe operating conditions employed in the process cause appreciable cracking of high boiling oils thereby producing olefinic fragments which, themselves, consume hydrogen, thereby lowering the process efficiency and increasing costs.

Alternate desulfurization processes that have been employed in the past have used alkali metal dispersions, such as sodium, as desulfurization agents. Basically, the process involves contacting a hydrocarbon fraction with a sodium dispersion, the sodium reacting with the sulfur to form dispersed sodium sulfide (Na_2S). However, such a process has not heretofore proven to be attractive, particularly for treatment of high boiling, high sulfur content feedstocks due to (a) the high cost of sodium, (b) problems related to removal of sodium sulfide formed in the process from the oil, (c) the impracticability heretofore of regenerating sodium from the sodium sulfide, (d) the relatively low desulfurization efficiency due, in part, to the formation, of substantial amounts of organo sodium salts, (e) a tendency to form increased concentrations of high mo-

lecular weight polymeric components (asphaltenes) in the oil, and (f) the failure to adequately remove metal contaminants (iron, nickel, vanadium) from the oil as is observed in the competitive catalytic hydrodesulfurization process.

Much thought has been given, in the past, to developing an economical method for separating the Na_2S from the oil and regenerating sodium metal therefrom. Fortunately, it has been found that facile separation of the Na_2S from the Na_2S -oil dispersion can be accomplished by treatment of the dispersion with water or hydrogen sulfide (H_2S).

In addition, it has been determined that the best approach to the problem of sodium regeneration would be to electrolyze an alkali metal salt that melts at about the same temperature as used for the desulfurization process and which can be electrolyzed with minimum consumption of electrical energy. The alkali polysulfides, preferably the sodium polysulfides, meet this requirement. There are three sodium polysulfides with melting points as follows: Na_2S_2 (885°F.), Na_2S_4 (545°F.) and Na_2S_5 (485°F.). These polysulfides are mutually soluble and intermediate compositions, having intermediate properties, can form. The eutectic is at about $\text{Na}_2\text{S}_{3.1}$ with a melting point of about 450°F. Moreover, the electrolysis of molten sodium polysulfide consumes less electrical energy than electrolyzing molten sodium chloride, the traditional electrolysis salt.

To this end, the separated Na_2S is treated with a sulfur-rich sodium polysulfide, thereby forming a sulfur-depleted sodium polysulfide having the desired composition which is then electrolyzed to regenerate sodium metal. The above-mentioned improvements to the alkali metal desulfurization process are disclosed in co-pending applications Ser. No. 256,547 and Ser. No. 256,438, both assigned to Esso Research and Engineering Company and filed on May 24, 1972.

In spite of the above-mentioned prior art improvements, low desulfurization efficiency has still remained an unsolved problem. It has been speculated that the low efficiency is due in part to the formation of organo-sodium compounds, formed either by reaction of the sodium with acidic hydrocarbons, addition of sodium to certain reactive olefins or as products obtained when sodium cleaves certain of the organic ethers, sulfides and amines contained in the oil. Formation of the organo-sodium compounds apparently desulfurization inactive materials themselves, has effectively removed a portion of the sodium which otherwise would be available for the desulfurization reaction. Sodium in excess of the theoretical amount for desulfurization must therefore be added to compensate for organo-sodium compound formation. Moreover, a hydrocarbon insoluble sludge which forms in the course of the sodium-treating reaction (apparently comprised mainly of organo-sodium compounds), makes the reactor mixture extremely viscous and hence impairs mixing and heat transfer performance in the reactor. Fortunately, the sludge decomposes when water or hydrogen sulfide is added preparatory to salt recovery and subsequent process steps are not complicated by the viscosity problem.

While sodium treating is particularly effective for removing sulfur from high boiling, high sulfur content (residua) feedstocks, it is ineffective for removing the metal contaminants (e.g., iron, nickel and vanadium)

found in these same feeds. Removal of the metals is desirable in that they contribute to slagging of refractories, corrosion of boiler tubes and turbine blades when the feeds are used as burner fuels. Furthermore, sodium treating has been shown to increase the high molecular weight polymeric compound content of the oil which is undesirable. Specifically, the oil is much more prone to sediment formation, as the high molecular weight fractions (asphaltenes) increase.

SUMMARY OF THE INVENTION

In accordance with this invention, it has now been discovered that an economically feasible desulfurization process vis-a-vis hydrodesulfurization of whole crude or residual oils can be achieved and that outstanding sulfur and metals removal can be realized without formation of reactor sludges or an increase in the high molecular weight polymeric fractions of the treated oil. Specifically, the process involves contacting a sulfur-containing petroleum oil stock with a desulfurization agent comprising an alkali metal, such as lithium, sodium, potassium and the like, preferably sodium, or an alkali metal alloy, preferably sodium/lead, at desulfurization conditions in the presence of a hydrogen-containing stream, thereby forming a mixture comprising an oil of diminished sulfur content containing alkali metal salts (generally in the form of a dispersion of submicron salts in the oil).

It is speculated that the effect of hydrogen addition on suppressing organo-metallic compound formation and in reducing the viscosity and asphaltene content of the product oil is directly related to the sodium desulfurization reaction. Specifically, it is thought that certain of the organic radicals produced by the attack of sodium on organic sulfur compounds present in the oil, will, in the absence of hydrogen, react further by the processes of dimerization and polymerization to yield a product oil with approximately the same or increased viscosity and asphaltene content relative to the feed. Furthermore, it is thought that the very stable, fused ring polyaromatic radicals produced by the attack of sodium on asphaltenic sulfur compounds react with alkali metal in a simple electron transfer reaction to yield the major portion of the organometallic, e.g., organosodium compounds. With hydrogen present it is thought that the radical reaction of hydrogen abstraction predominates thereby minimizing the reactions which yield polymers and organo-metallic compounds. It is also considered likely that hydrogen also decomposes organo-metallic compounds derived from other sources, e.g., reaction of the alkali metal with acidic hydrocarbons. The role played by hydrogen in promoting demetallization (iron, nickel, vanadium) of the oil is not fully understood at the present time.

The hydrogen partial pressure in the desulfurization zone can range from about 25 to 800 psig, preferably 100 to 200 psig, e.g., 150 psig.

It is noted that either pure hydrogen or dilute "low value" hydrogen such as that obtained from refinery discard streams, e.g., the gases discarded after hydrotreating processes, gas effluent from cat cracker light ends facilities, or powerformer recycle hydrogen streams, may be used as the hydrogen source in the subject process. From an economic standpoint, it is preferable to use the dilute "low value" hydrogen where possible.

Hereinafter the invention will be described with respect to sodium although it is understood that other alkali metals, as hereinbefore disclosed, may be used. Subsequent to the desulfurization step, the oil-salt mixture is contacted with either H₂S or water as disclosed in copending applications Ser. No. 256,547 and Ser. No. 256,438, both filed May 24, 1972, thereby substantially separating a salt phase from the oil phase. The salts are recovered using any conventional recovery technique, such as filtration or centrifugation. At least a portion of the recovered salts are then contacted with a sulfur-rich sodium polysulfide thereby yielding a sulfur-depleted sodium polysulfide which is subsequently electrolytically dissociated to form sodium metal which may be used in the initial desulfurization step.

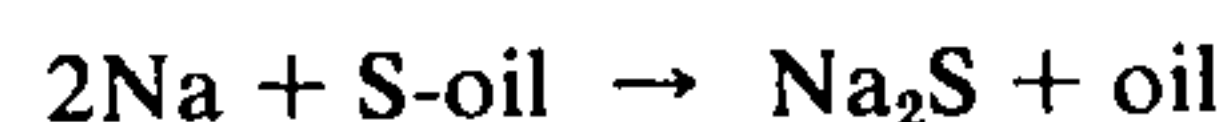
Any feedstock from which sulfur is desired to be removed may in theory be used in the instant process. Thus, for example, suitable feedstocks include whole crude such as Safaniya crude (Middle East), Lagunillas crude (Venezuelan), or U.S. crudes, residual fractions or any distillate fraction. The subject process is particularly adapted to the desulfurization of whole crude or residua that are difficult to treat by other methods such as hydrodesulfurization.

While the feedstock may be fed directly to the initial contacting zone for desulfurization without pretreatment, it is desirable to desalt the feed in order to prevent NaCl contamination of the molten polysulfide feed to the electrolysis cell. Desalting is a well-established process in the industry. A particularly preferred desalting process involves the addition of a small amount of water to the oil in order to dissolve the salt contained therein, followed by electrical coalescers. The oil is then dehydrated by conventional means known in the industry.

The sodium may be used as a dispersion of the pure metal or in the form of a molten alloy such as sodium/mercury, sodium/lead or sodium/tin. When sodium/lead is the alloy, desirable proportions comprise about 0.3 to about 0.5 g.-atom sodium/0.7 to about 0.5 g.-atom lead, and when using sodium/tin, about 0.2 to 0.3 g.-atom sodium/0.8 to 0.7 g.-atom tin.

The contacting of the sodium metal or sodium metal alloy with the sulfur-containing oil is preferably carried out at temperatures and pressures sufficient to maintain the bulk of the reactants within the reaction zone in the liquid phase. However, conditions may be varied to provide phase contact. The reaction temperature will generally be maintained between about 450° and 750°F., preferably 600° to 700°F., e.g., 650°F. The reaction pressure will depend on the feed temperature employed and the desired hydrogen pressure. For reduced crude fractions the total pressure will range between about 35 and 300 psig, preferably 100 to 200 psig. For whole or topped crude, pressures may be raised to as high as about 500 to 600 psig in order to maintain all or most of the oil in the liquid phase.

The sodium metal reacts with the sulfur-containing oil stock as shown in equation 1 below to yield sodium sulfide which generally forms as a microcrystalline dispersion in the oil.



(1)

By-product salts such as organometallic salts, metal mercaptides, metal oxides and the like may also form. In addition, organo-oxygen contained in the feedstock

is removed therefrom by reacting with the sodium metal. (Typical crudes contain between about 0.1 and 0.2 percent organic oxygen). Furthermore, depending on the amount of water present in the feed and the reaction conditions, varying amounts of thiosulfate, hydroxide and salts of organic acids may be formed. Additionally, some organo-nitrogen is also removed from the oil by reaction with the sodium.

The desulfurization step is conducted as a batch or continuous type operation but is preferably continuous. In general, the various means customarily employed in extraction processes to increase the contact area between the oil stock and the sodium metal or alloy thereof can be employed. The apparatus used in the desulfurization step is of a conventional nature and can comprise a single reactor or multiple reactors equipped with (a) shed rows or other stationary devices to encourage contacting; (b) orifice mixers; (c) efficient stirring devices such as mechanical agitators, jets of restricted internal diameter, turbomixers and the like, or (d) a packed bed.

The petroleum oil stock and the sodium metal or sodium metal alloy can be passed through one or more reactors in concurrent, crosscurrent, or countercurrent flow, etc. It is preferable that oxygen and water be excluded from the reaction zones; therefore, the reaction system is thoroughly purged with dry nitrogen and the feedstock dried prior to introduction into the reactor. It is understood that trace amounts of water, i.e., less than about 0.5 weight percent, preferably less than about 0.1 weight percent based on total feed, can be present in the reactor. Where there are larger amounts of water, process efficiency will be lowered somewhat as a consequence of sodium reacting with the water. The resulting oil dispersion is subsequently removed from the desulfurization zone and contacted with either water or H_2S as described in more detail below.

WATER-TREATMENT STEP

The water is added to the oil-salt mixture, in one embodiment of the invention (hereinafter referred to as Scheme A), in amounts ranging between about 10 and 80 mole percent, based on total number of moles of salt present in the mixture. In a second embodiment of the invention (hereinafter referred to as Scheme B), about 110–200 mole percent H_2O is added to the mixture. The net consequence of the water treatment step is (1) to convert at least a portion of the sodium salts (other than sodium sulfide and sodium mercaptides which are essentially non-reactive with water under the reaction conditions) to $NaOH$ and (2) to agglomerate submicron salts to yield a macrocrystalline salt phase (preferably having a particle size between about 150 and 500 microns) which readily disengages from the oil phase.

The amount of water added to the oil-salt mixture determines, in part, the size of the salt particles which separate from the oil. Thus, for example, a larger particle agglomerate size (comprising in part a hydrate of Na_2S) is formed using Scheme B, vis-a-vis Scheme A wherein a minimum amount of water is used to disengage the salts from the oil. Contacting conditions in the former case, i.e., Scheme A comprise (1) a temperature of at least about 610°F. and ranging between about 610° and 800°F., preferably between about 650° and 750°F. and most preferably at the temperature of the desulfurization step, and (2) a pressure ranging between about atmospheric pressure and 100 psig.

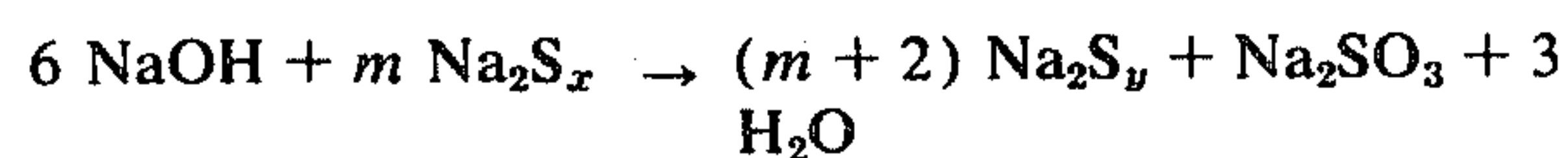
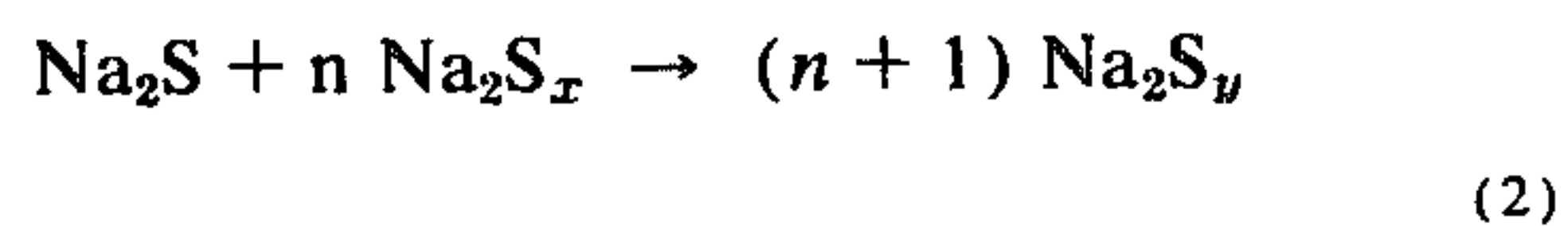
With regard to Scheme B, temperatures during the water addition step are maintained within the range of about 500° and 650°F. Typical pressures employed vary between about 100 and 500 psig, preferably between about 100 and 200 psig. The latter pressures reflect the partial pressure of the excess water vapor present in the contacting zone. It is important to note that at the elevated temperatures used in Scheme B, the salt mixture does not separate from the oil. The mixture must first be cooled to a temperature below about 250°F. in order to agglomerate the salts.

In general the salt composition after water treatment comprises a major amount of $NaOH$ and Na_2S and a minor amount of other components such as sodium mercaptides, which as mentioned supra, are unreactive with the water under the reaction conditions. Separation of the salt phase from the oil phase can take place using any one of several well-known commercial techniques such as filtration or centrifugation.

In the case of Scheme B, the cost disadvantages related to cooling the salt phase to a temperature below 250°F. will have to be balanced with the increased ease of separation of the salt-oil mixture related to increased particle size of the salt agglomerate vis-a-vis Scheme A, in determining the amount of water to use in a particular operation.

After separation of the salts from the oil, e.g., by filtration, the salts are contacted with a sulfur-rich sodium polysulfide, desirably in the molten state and preferably represented by the formula, Na_2S_x (where x varies from about 4.0 to 4.9, preferably from about 4.4 – 4.8, most preferably from about 4.5 to 4.7) and H_2S . The contacting results in the formation of a sulfur-depleted sodium polysulfide, i.e., Na_2S_y (where y ranges from about 2.8 to 4.5, preferably from about 3.5 to 4.3, most preferably from about 4.0 to 4.2, e.g., 4.0), desirably at a temperature above the melting point of the resulting polysulfide.

The reaction of Na_2S_x with the major components of the salt mixture, i.e., $NaOH$ and Na_2S , is thought to proceed by the following generalized equations:



The values of n and m (moles of polysulfide) in the above equations will depend on the values chosen for x and y . The amount of Na_2S_x that is required to react with the H_2O -treated salt mixture varies, being dependent in part on the amounts of Na_2S and $NaOH$ present in the salts and on the compositions of both the sulfur-rich polysulfide and the sulfur-depleted polysulfide. Using the above equation, the amount of Na_2S_x required to react with a salt mixture comprising, for example, 1 mole of Na_2S , i.e., n and 1 mole of $NaOH$, i.e., m is:

$$\text{Moles } Na_2S_x \text{ to react with 1 mole of } Na_2S = y - 1/x - y \quad (4)$$

$$\text{Moles } Na_2S_x \text{ to react with 1 mole of } NaOH = (1 + 2/y/x - y) 1/6 \quad (5)$$

where:

y = the number of sulfur atoms in Na_2S_y

x = the number of sulfur atoms in Na_2S_x

Knowing the number of moles of Na_2S and $NaOH$ present in the salt mixture and the values for x and y , the

required amount of Na_2S_x can be determined. It is noted that the calculated amounts of Na_2S_x are minimum values, and that larger quantities may be required depending on the amount of other salts that may be present in the salt mixture, which salts also react with the Na_2S_x .

The Na_2SO_3 that forms, as shown in equation 3, can be converted to polysulfide by contact with H_2S . In addition, sodium mercaptides and any residual oxygen-bearing salts such as NaOH and the like present in the sodium polysulfide-treated mixture are converted to polysulfide by the same H_2S treatment. In general about 0.5 – 1.0 moles of H_2S per mole NaOH in the salt mixture is sufficient to effect the desired conversion, although larger amounts may be used if desired. The H_2S treatment may take place before, during or after the polysulfide contacting step.

The Na_2S_y is subsequently electrolyzed in an electrolytic cell as more fully described below. Small amounts of sodium compounds may still be present in the oil after salt separation and may be removed by contacting the oil with an acid such as H_2S , acetic acid, dilute sulfuric acid and the like. Treatment of the water-treated salt mixture with sulfur-rich sodium polysulfide and H_2S results in the formation of a sulfur-depleted sodium polysulfide.

H_2S TREATMENT OF THE OIL-SALT MIXTURE

As an alternative to the above-described water treatment, the oil-salt mixture from the sodium desulfurization step can be contacted with H_2S in amounts ranging from about 10 to about 100 mole percent, based on the total number of moles of salt present in the mixture, preferably 30 to 60 mole percent. The net consequence of the H_2S treatment is twofold (1) at least a portion of the by-product sodium salts such as sodium oxide, sodium hydroxide and the like are converted to sodium hydrosulfide, and (2) submicron salts are agglomerated to yield a macrocrystalline salt phase (preferably having a particle size between about 150 and 200 microns) which readily disengages from the oil phase. The salt phase is separated from the oil phase and recovered employing one of several well-known commercial techniques, notably filtration or centrifugation. The H_2S -treated mixture of salts is then contacted with a sulfur-rich sodium polysulfide, desirably in the molten state and preferably represented by the formula, Na_2S_x (where x varies from about 4.0 to 4.9, preferably from about 4.4 to 4.8, most preferably from about 4.5 to 4.7). The contacting results in the formation of a sulfur-depleted sodium polysulfide, i.e., Na_2S_y (where y ranges from about 2.8 to 4.5, preferably from about 3.5 to 4.3, most preferably from about 4.0 to 4.2), desirably at a temperature above the melting point of the resulting polysulfide. This recovery and conversion method will be hereinafter referred to as Scheme C.

Alternatively, the H_2S -treated mixture of salts in oil i.e., without salt separation from the oil, can be contacted directly with the molten polysulfide (Na_2S_x) thereby converting at least a portion of the salts in situ to a sulfur-depleted polysulfide, Na_2S_y , which is preferably in a molten state (Scheme D). It is preferable that the value of y in the sulfur-depleted polysulfide Na_2S_y be in the range of about 2.8 to 3.5 in order to avoid back-sulfiding of the oil phase by the polysulfide.

In a second embodiment of the invention (Scheme E) an excess amount of H_2S is added to the sodium sulfide/oil mixture thereby converting the sodium sulfide

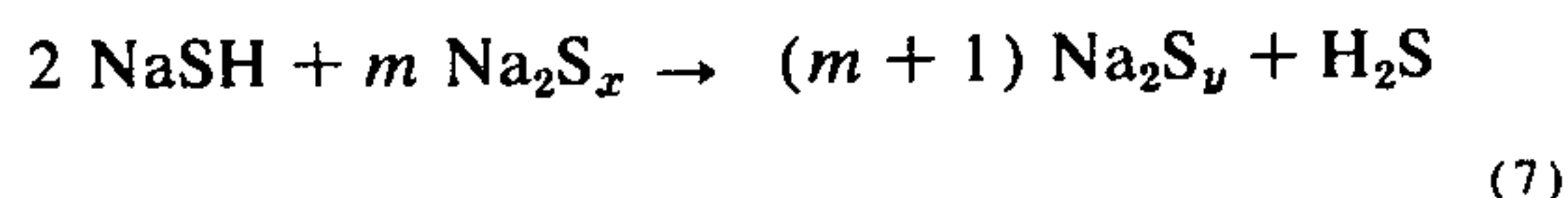
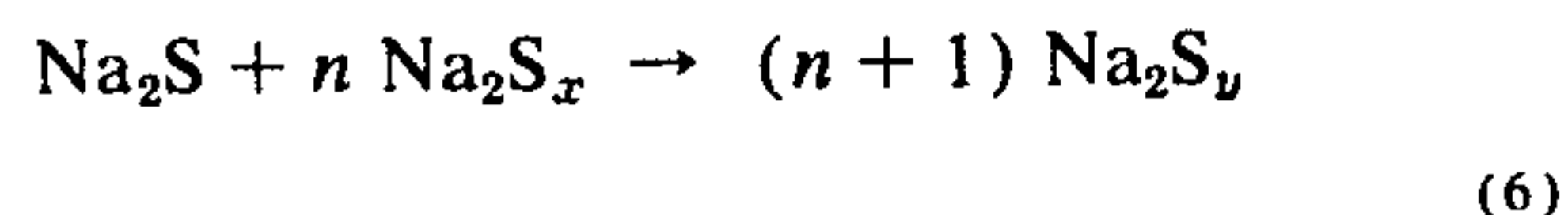
(and other sodium salts present therein) to sodium hydrosulfide (NaSH). The amount of hydrogen sulfide added can range from about 110 mole percent based on the total number of moles of salt present in the oil up to about 400 mole percent, but is preferably used in amounts ranging from about 120 to 160 mole percent. At the contacting temperature employed, the NaSH is substantially molten and is readily separable from the oil. Thereafter, the NaSH is contacted with either Na_2S_x or sulfur to form Na_2S_y which is electrolyzed to form sodium.

Thus, it has been surprisingly discovered that contacting the oil/salt mixture with 10–400 mole % H_2S , based on total moles of salt present in the mixture, results in a facile disengagement of the alkali metal salts from the oil.

It is also possible, and, perhaps, desirable, to convert NaSH to Na_2S_y by contact with molten sulfur rather than the molten polysulfide Na_2S_x . According to this procedure, (Scheme F) molten sulfur obtained from pyrolysis of the electrolysis product, Na_2S_z , is added to the oil-free, molten NaSH stream. Normally, sufficient sulfur is added to give the desired electrolysis feed, i.e., Na_2S_y , where y ranges from about 3.5 to 4.3.

It should be noted that in each of the foregoing schemes for the recovery and conversion of desulfurization salts, that hydrogen sulfide is liberated when the H_2S -treated salts are contacted with sulfur-rich sodium polysulfide or elemental sulfur. The hydrogen sulfide is recovered, purified to remove traces of water and recycled in the process.

The amount of Na_2S_x that is required to react with the H_2S -treated salt mixture varies and is dependent on the compositions of both the sulfur-rich polysulfide and the sulfur-depleted polysulfide. The reaction of Na_2S_x with either Na_2S or NaSH is thought to proceed as follows:



From the above stoichiometry, it is seen that the same amount of Na_2S_x is required to react with NaSH as with Na_2S to yield the same quantity of Na_2S_y . The values of n and m in the above equations will depend on the values chosen for x and y . Using the equations, the amount of Na_2S_x required to react with a salt mixture comprising 1 mole of Na_2S , i.e., n , and 1 mole of NaSH , i.e., m is:

$$\text{Moles } \text{Na}_2\text{S}_x \text{ to react with 1 mole of } \text{Na}_2\text{S} = y - 1/x - y \quad (8)$$

$$\text{Moles } \text{Na}_2\text{S}_x \text{ to react with 1 mole of } \text{NaSH} = \frac{1}{2} (y - 1/x - y) \quad (9)$$

where:

y = the number of sulfur atoms in Na_2S_y

x = the number of sulfur atoms in Na_2S_x

Knowing the number of moles of Na_2S and NaSH present in the salt mixture and the values for x and y , the required amount of Na_2S_x can be determined. It is noted that the calculated amounts of Na_2S_x are minimum values and that larger quantities may be required depending on the amount of other salts that may be present in the salt mixture which also react with the Na_2S_x .

After further treatment of the Na_2S_y (formed by any one of Schemes C-F) to remove various impurities

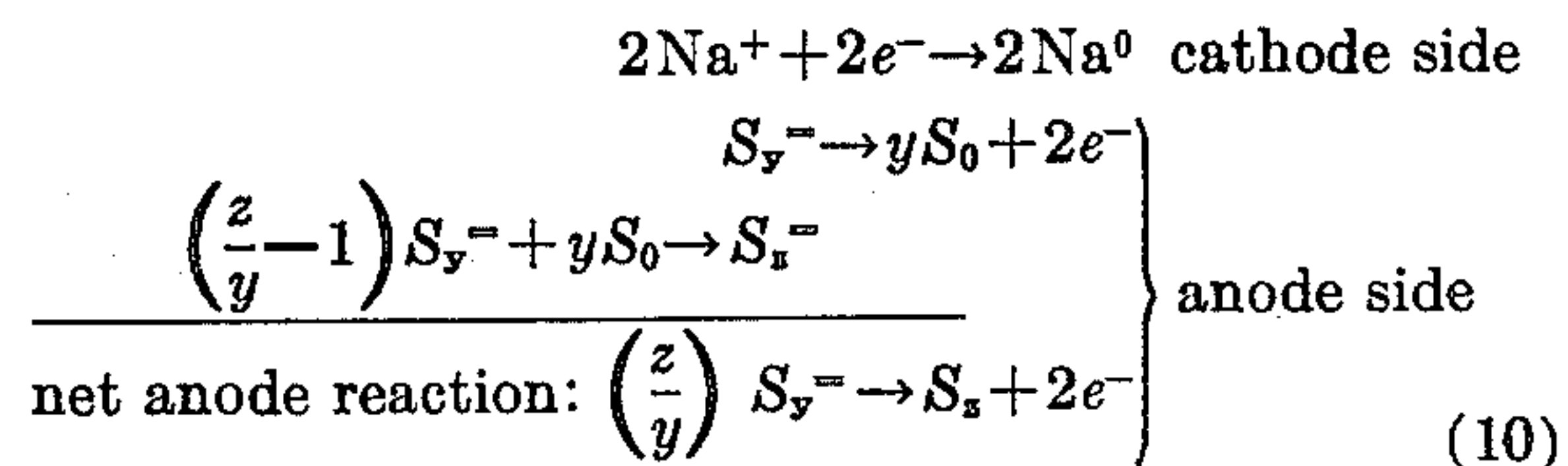
present therein, the Na_2S_z is cycled to electrolytic cells wherein it is dissociated to form molten sodium and a sulfur-rich sodium polysulfide, i.e., Na_2S_z wherein z ranges from about 4.5 to 5.0, preferably from about 4.6 to 4.9, most preferably from about 4.7 to 4.9. The sodium thereby formed is then withdrawn and either alloyed with a molten metal such as lead or tin or introduced directly into the desulfurization zone in undiluted form.

As a less preferred alternative to the above recovery processes, the sodium treated oil-salt mixture can be contacted with an acid, preferably acetic acid, thereby converting a substantial portion of the salts to sodium acetate, which separates from the mixture, and liberating H_2S . In general, the salt mixture is first diluted with a solvent such as toluene and then treated with acetic acid, preferably an excess amount, e.g., 110–130 mole percent, based on moles of sodium present in the oil. After heating the resulting said mixture, such as on a steam bath, the mixture is filtered to recover salt-free product.

The electrolytic cell unit may preferably comprise a sodium ion-conducting physical and electronic barrier or membrane that separates alkali metal on the one side from alkali metal polysulfide on the other side. Generally, the membrane may be composed of any material that can function as a sodium ion-conducting separator; however, beta-alumina containing sodium oxide is preferred. Such beta-alumina will contain sodium oxide in the general range of about $\text{Na}_2\text{O} \cdot 11\text{Al}_2\text{O}_3$ – $\text{Na}_2\text{O} \cdot 5\text{Al}_2\text{O}_3$. It is noted that when an alkali metal other than sodium is employed in the instant process, the oxide of the alkali metal will be admixed with the beta-alumina in lieu of Na_2O .

The beta-alumina may be used in the pure form or doped with a small amount of metal oxide such as MgO , Li_2O and the like. A detailed discussion of doped beta-alumina is provided in an article appearing in the Electrochemical Society Extended Abstracts — Los Angeles Meeting — May 10–15, 1970, entitled "Ionic Conduction in Impurity Doped β -alumina," by Atsuo Imai et al., the disclosure of which is incorporated herein by reference. Reference is also made to U.S. Pat. No. 3,488,271 to J. T. Kummer et al. and U.S. Pat. No. 3,475,225 to G. T. Tennenhouse. During cell operation, sodium ions migrate from the sodium polysulfide side, i.e., the anode side, through the barrier to the sodium metal side, i.e., the cathode side, where they are neutralized by electrons. At the same time polysulfide ions give up their electrons at the electron-conducting anode to form elemental sulfur that then reacts with additional polysulfide anions to form new polysulfide ions, i.e., S_z^- , of greater sulfur content.

As indicated above, z will take values in the range of about 4.5 to 5.0. The S_z^- anions are continually removed from the cell in combined form with sodium, i.e., Na_2S_z . The anode may comprise any suitable electron conducting-current collector such as graphite, molybdenum, titanium, chromium, stainless steel, or aluminum that can withstand corrosive attack of the sodium polysulfide. The cells are arranged preferably in series electrically, so that the anode for one cell is the cathode for the one adjacent to it. The overall reaction is shown below:



The recovered Na_2S_z can be reduced in sulfur content to Na_2S_x (the latter being contacted with the H_2S -treated salt mixture as described supra) by application of a vacuum and/or heat thereby liberating sulfur corresponding to that which was removed from the oil. Alternatively, at least a portion of the Na_2S_z may be contacted directly with the H_2S -treated salt mixture.

In other embodiments, elemental sulfur is allowed to build up in the cell and the operating temperature therein is maintained high enough so that the sulfur is continuously removed therefrom as vapor. In another embodiment liquid sulfur forms in the cell and is separated from the polysulfide outside the cell. In yet another embodiment, the sodium/lead alloy may be formed internally, i.e., in situ, before the molten sodium metal is withdrawn from the electrolytic cell by continuously feeding lead or spent sodium/lead alloy to the cathode side of the cell.

While a beta-alumina type cell has been described, any other cell that is capable of economically decomposing sodium polysulfide into molten sodium is sufficient for the present purposes. A particular beta-alumina electrolytic cell and methods for the preparation of beta-alumina are described in such patents as U.S. Pat. No. 3,488,271 and 3,404,036 to J. T. Kummer et al., U.S. Pat. No. 3,468,709 to J. T. Kummer and U.S. Pat. No. 3,446,677 and U.S. Pat. No. 3,475,225 to G. T. Tennenhouse, the disclosures of which are incorporated herein by reference.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a flow diagram of the overall desulfurization process using sodium metal in pure form and H_2S as the dispersing agent. Desulfurization salts are recovered from the oil according to Scheme C.

FIG. 2 shows the reactor system for desulfurization with an alloy of sodium, i.e., sodium/lead.

FIG. 3 shows the changes required to operate the process using salt recovery Scheme D.

FIG. 4 shows the steps used in salt recovery Schemes E and F.

FIG. 5 is a flow diagram of the overall desulfurization process using sodium metal in pure form and water as the dispersing agent, via Schemes A or B.

FIG. 6 is a simplified scheme showing the formation of the molten sodium within the electrolytic cell.

Referring to the drawings in detail, the desulfurization reactor systems used in the instant process vary depending on whether sodium or sodium alloy is used as the reactant. The system using sodium will be described first, then the system using sodium alloy.

Turning now to FIG. 1 (wherein H_2S is the agglomerating agent) and the description of Scheme C, a sulfur-containing feedstock, preheated to 450°–500°F., is fed by means of line 1 and pump 2 to separator vessel 3 where trace amounts of water and light hydrocarbon fractions are removed through line 4. The feed is then discharged through line 5 by pump 6 to filter vessel 7

wherein particulate matter, i.e., coke, scale, etc. is removed.

The feed is preliminarily desalted by conventional means (not shown). Feed exiting the filter via line 8 is split into two streams. A small portion is fed through line 9 and heat exchanger 14 to dispersator vessel 11 where a dispersion is formed with sodium entering through line 67. The dispersator vessel is of a conventional design and is operated at 250°–300°F. at atmospheric pressure. The vessel is blanketed with nitrogen. The resultant dispersion, drawn through line 12, blends with the balance of the feed in line 10 and enters the charging pump 13, where the pressure is raised to about 500 psig, for whole crudes and distillates and about 50 psig for residual fuels. The feedstock will ordinarily be a whole crude of about 1 to about 3 weight percent sulfur based on total feed or a residual stock of about 2 to about 7 weight percent sulfur based on total feed, although distillate stocks can be used.

The oil enters heat exchanger 16 via line 15 where the temperature is raised to about 500° to 550°F. and is then fed through line 17 to reactor vessel 18. The reactor contains baffles 19 to promote continuing contact between sodium and the oil and to prevent bypassing from the inlet to the outlet. Low pressure hydrogen is introduced into the reactor vessel 18 via line 74 in amounts such that the total partial pressure of hydrogen in the reactor ranges between about 25 and 500 psig. Holding time in the reactor is about 15 to 60 minutes and is preferably 30 minutes. The temperature at the top of reactor 18 is about 680°F. Gas that is formed due to the increase in temperature and excess hydrogen is taken overhead through line 20 and is condensed and depressurized by conventional means (not shown). The desulfurized oil containing dispersed sodium sulfide and other salts leaves the top of reactor 18 via line 21.

The remainder of FIG. 1 will be explained below after describing the alternate reactor system for sodium alloy shown in FIG. 2.

FIG. 2 shows the reactor system for the case where sodium alloy is used. It differs from the case where sodium alone is used primarily, in that oil is recycled to the reactor in order to prevent cooling of the alloy below its melting point and in order to recover and recycle the spent alloy. The feedstock which has been preliminarily preheated, dehydrated and desalted as per FIG. 1 is premixed in line 17 with desulfurized recycled oil from pump 68. The mixed oil stream enters reactor vessel 69 via line 17 and flows in an upward direction therethrough. Low pressure hydrogen is introduced into reactor vessel 69 via line 74. The vessel is of such a size that the oil remains in the reaction portion below the sodium alloy disperser 70 for about 10 minutes to about 1 hour. The sodium alloy, preferably sodium/lead or sodium/tin or a mixture of the two, enters reactor 69 via disperser 70. Atom compositions of about 0.3 to 0.5 Na/0.7 to 0.5 Pb or 0.2 to 0.3 Na/0.8 to 0.7 Sn are suitable.

The alloy droplets comingle with the rising oil stream and being heavier than the oil and of large enough size, fall downwardly through the rising oil stream. Baffles 71 promote contact. The spent alloy collects in the bottom of reactor 69 and passes via line 72 to the alloy storage vessel 73. The alloy is fortified by contact with freshly regenerated sodium entering vessel 73 via line 67. Pump 75 feeds the fortified alloy via line 76 to disperser 70.

The dispersed oil passes into a settler zone located in the top of reactor 69 where any small, entrained alloy particles are allowed to settle. Baffles 77 act as collecting plates for the alloy particles and are placed at a slight angle so that the coalesced alloy can run off the ends. The desulfurized oil/sodium sulfide dispersion leaves reactor 69 via line 21.

One particular reactor system has been described. However, the alloy and oil can flow cocurrently, and any one of several well-known types of mixers such as pump mixers, high shear mixers or paddle blade mixers and the like can be employed. Other settling means, in particular external, long, horizontal flow vessels or liquid cyclones and the like can be also used.

Sodium sulfide-oil dispersion in line 21 is introduced into contacting vessel 22 wherein the said dispersion is contacted with 30–80 mole percent hydrogen sulfide based on the total moles of salts contained in the oil, at a temperature between about 600°–800°F., preferably 625°–750°F., e.g. 700°F., and most preferably at the temperature of the desulfurization step. The pressure is maintained between about 25–50 psig. Hydrogen sulfide is introduced into said contactor via line 23. Residence time in the contactor vessel is on the order of about 10 minutes, although longer or shorter times may be used if desired.

The H₂S-treated dispersion exits through line 24 at about 700°F., and 25–100 psig and is then cooled to about 450°F in heat exchanger 25. The mixture is then fed through line 26 to hydroclone vessels 27 and 28 in series. Desulfurized oil is withdrawn via line 29 to heat exchanger 30 and exits at 250°–300°F. through line 31. An acid, such as dilute sulfuric acid or acetic acid, may be injected into line 31 through line 32 to react with oil-soluble sodium salts, e.g., sodium mercaptides and the like and the resultant mixture enters the electrostatic precipitator 34 via line 33. The acidic aqueous phase from vessel 34 is withdrawn through line 36 and discarded. Desulfurized oil is fed through line 35 to steam stripper 37 and subsequently to storage via line 38.

Oil-salt slurry drawn from the hydroclone vessels through lines 39 and 40 is fed to wash vessel 41 where a light hydrocarbon wash, entering through line 42, is used to remove heavy adhering oil. The wash effluent is drawn off through line 43 and is eventually fractionated to recover the desulfurized oil content and the light hydrocarbon. The wash vessel operates at 25–100 psig at temperatures of 150°–300°F. A slurry of washed solids is fed through line 44 to drier 45 to remove light hydrocarbon, which is taken off through line 46.

Dry solids are fed to blending vessel 48 via line 47, wherein contact is made with sulfur-rich polysulfide (Na₂S_x as hereinabove described) that enters the vessel through line 49. The contacting is conducted at a temperature of about 500 to 820°F., preferably 600°–800°F., most preferably from about 650°–750°F., e.g., 700°F., and at a pressure between about atmospheric pressure and 100 psig, preferably between atmospheric pressure and 50 psig. Hydrogen sulfide released in the blending reaction along with some small amount of light hydrocarbon is removed through line 50, blended with makeup hydrogen sulfide entering from line 51 and is recycled to vessel 22 by way of line 23.

The molten sulfur depleted polysulfide (Na₂S_y as hereinabove defined) formed by the reaction of H₂S-

treated salts with sulfur-rich polysulfide is removed from blending vessel 48 through line 52 and fed to filter vessel 53 to remove particulate matter such as coke and melt insoluble salts. Line 54 is used to purge a small stream of sodium polysulfide from the system in order to prevent buildup of impurities to an inoperable level.

These dissolved impurities arise from the feed and from equipment corrosion as well as from the organo-metallic compositions removed from the feed by the action of sodium. Specifically, compounds containing combined iron, vanadium, silica, nickel, chromium, lead and tin may form and are removed from the system via line 54.

In addition to the above-mentioned impurities, Na_2CO_3 , Na_2SO_3 and the like may also be present in the polysulfide. With the exception of Na_2CO_3 (which can be removed by $\text{Ca}(\text{OH})_2$ treatment), these impurities can be removed by treatment with H_2S , thereby converting at least a portion of the impurities to polysulfide. Treated Na_2S_y is introduced into cell 56 via line 55.

The process incorporating salt recovery Scheme D is illustrated by reference to FIG. 3. The hydrogen sulfide-treated oil-salt dispersion removed from contactor vessel 22 is fed through line 26 to scrubbing tower 80 wherein it is contacted countercurrently with molten sodium polysulfide (Na_2S_x) that is introduced via line 95.

The tower is divided into a series of stages by porous plates 81 and is maintained at a temperature ranging from about 500° to 800°F., preferably 650° to 700°F., and a pressure ranging from about 50 to 500 psig, preferably about 50 to about 100 psig. The sodium sulfide dispersed in the oil reacts with the sodium polysulfide to yield a molten sulfur-depleted polysulfide (Na_2S_y , wherein y varies from 2.8 to 3.5), which drops from the oil and collects at the tower bottom. If necessary, additional hydro-sulfide can be added to the melt through line 91 to effect conversion of by-product salts to the sodium polysulfide.

While the polysulfide contacting step has been shown here to be continuous, it may also be conducted as a batch operation. In general, the various means customarily employed in extraction processes to increase the contact area between the various materials can be employed. The apparatus is of a conventional nature and can comprise a single reactor or multiple reactors equipped with efficient stirring devices such as mechanical agitators, jet of restricted internal diameter, turbomixers and the like. The sodium polysulfide, i.e., Na_2S_x and the oil/sodium sulfide mixture can be passed through one or more reactors in concurrent, crosscurrent or countercurrent flow.

Excess hydrogen sulfide, hydrogen sulfide liberated in the $\text{Na}_2\text{S}_x - \text{NaSH}$ reaction and liberated water are removed from the reactor through line 50. After suitable drying (not shown) the hydrogen sulfide stream is recycled to the contactor vessel 22. As in the preceding case, desulfurized oil exits via line 29 for further processing and storage.

The molten sulfur-depleted polysulfide (Na_2S_y , where y varies from 2.8 to 3.5) removed from the tower via line 96 is split into two parts. One portion is fed through line 94 to blend with a portion of the sulfur-rich polysulfide product entering from line 93. The ratio of sulfur-rich and sulfur-depleted polysulfide will be regu-

lated by the value of x in the desired scrubbing agent, Na_2S_x . The remaining sulfur-depleted polysulfide in line 97 is blended with the remaining sulfur-rich polysulfide entering from line 92 and the resultant mixture is fed via line 52 to the electrolytic cells 56.

The process incorporating salt recovery Scheme E is illustrated by reference to FIG. 4. According to this scheme, an excess amount (110–160 mole percent based on total salts contained in the oil) of hydrogen sulfide is added to the oil-salt dispersion in vessel 22 at a temperature of about 670°–800°F., preferably 680°–750°F. and at a pressure of about 50–500 psig, preferably 100–200 psig. The resultant mixture is then fed via line 26 to the settler vessel 82 which operates at conditions similar to those used in vessel 22. Residence time is on the order of 5 to 30 minutes, preferably about 15 minutes. Molten sodium hydrosulfide separates from the oil, collects at the bottom of the settler and is drawn off through line 83 which feeds directly to the polysulfide blending vessel 48 as noted in FIG. 1. Subsequent steps are identical to those described in FIG. 1. The product oil is withdrawn through line 29 and is processed according to Scheme A of FIG. 1.

The process variation noted as Scheme F is illustrated in FIG. 4. Molten sodium hydrosulfide is withdrawn from settler vessel 82 and fed via lines 83 and 84 to blending vessel 86, where it is contacted with molten sulfur (line 85) at a temperature between 500°–800°F., preferably between 600° and 700°F. and at a pressure between atmospheric pressure and 100 psig, preferably between atmospheric pressure and 50 psig, rather than molten sodium polysulfide, Na_2S_x . The mole ratio of sulfur to NaSH is maintained in the range of 1:1 up to 3:1 but preferably at 1.5 to 2.0.

The sodium polysulfide product, i.e., Na_2S_y , withdrawn through line 99, is blended with pyrolyzer polysulfide product (Na_2S_x) and fed via line 52 to the electrolytic cells (not shown). Liberated hydrogen sulfide is taken overhead through line 50 and is ultimately recycled to contacting vessel 22. The pyrolyzer vessel 60 is operated at conditions relatively more severe than those used in Scheme A in order to furnish the volume of sulfur required.

Turning to FIG. 5 (wherein water is used as an agglomerating agent), the process shown therein is generally similar to that described in FIG. 1 with the following modifications. Specifically, the oil-salt dispersion enters contactor vessel 22 via line 21 and is treated, in one embodiment of the invention (Scheme A), with 30–80 mole percent water (based on total moles of salt contained in the oil). Water enters through line 23. The contact vessel operates at 610°–800°F., preferably 650°–700°F., most preferably at the desulfurization temperature, and at a pressure of about 15 to 100 psig. Residence time in the vessel is on the order of 10 minutes, although longer or shorter times may be used if desired. The resulting mixture is fed via line 24 to heat exchanger 25 where the temperature is dropped to about 400°–450°F. and then via line 26 to the hydroclone vessels 27 and 28, which are operated in series.

Desulfurized oil is withdrawn via line 29 to heat exchanger 30 and exits at 250°–300°F. through line 21. An acid such as dilute sulfuric acid or acetic acid, may be injected into line 31 through line 32 to react with oil-soluble salts, e.g., sodium mercaptides and the like, and the resultant mixture enters the electrostatic precipitator 34 via line 33. The acidic aqueous phase from

vessel 34 is withdrawn through line 36 and discarded. Desulfurized oil is fed through line 35 to steam stripper 37 and subsequently to storage via line 35.

In another embodiment of the invention (Scheme B), 110–200 mole percent water (based on total moles of salt contained in the oil) is added to the oil-salt dispersion in contactor vessel 22. The temperature is maintained within the vessel, at about 500°–650°F. and at a pressure of about 100 to about 500 psig. Withdrawal of the resultant mixture followed by cooling of same (such as by heat-exchange) to a temperature below about 250°F., results in the formation of large sized particles of salt, presumably the hydrated Na_2S . In fact the particles are so large and the settling rate so rapid that hydroclone action may not be necessary.

Salt slurries drawn from the hydroclones through lines 39 and 40 are washed free of adhering oil in vessel 41 with a light hydrocarbon which enters through line 42. The resultant washed salts enter drier 45 through line 44 where light hydrocarbon and traces of water are removed at about 550°–700°F. The dried salts enter the blending vessel 48 where contact is made with molten sodium polysulfide entering through line 49. The resultant melt is further reacted with hydrogen sulfide entering from line 51. Hydrogen sulfide, it is thought, converts oxygen-bearing salts, e.g., NaOH , Na_2SO_3 , to the desired polysulfide and liberates the oxygen in the form of water. Excess hydrogen sulfide, light hydrocarbons and water exit the blending vessel via line 50. Eventually the components of the stream are resolved (method not shown) and the hydrogen sulfide is recycled to vessel 48.

The molten sulfur-depleted polysulfide (Na_2S_x as hereinabove defined) formed by the reaction of H_2O -treated salts with sulfur-rich polysulfide is removed from blending vessel 48 through line 52 and fed to filter vessel 53 to remove particulate matter such as coke and melt insoluble salts. Line 54 is used to purge a small stream of sodium polysulfide from the system in order to prevent buildup of impurities to an inoperable level.

These dissolved impurities arise from the feed and from equipment corrosion as well as from the organo-metallic compositions removed from the feed by the action of sodium. Specifically, compounds containing combined iron, vanadium, silica, nickel, chromium, lead and tin may form and are removed from the system via line 54. Treated Na_2S_x is then introduced into electrolytic cells 56 via line 55.

A dry nitrogen stream (not shown) blankets the electrolytic cells. The electrolytic cells are of a conventional design and may comprise any cell capable of converting the polysulfide to sodium metal. Preferably, the individual cell unit comprises a molten sodium-containing cavity and a molten sodium polysulfide-containing cavity separated from each other by a sodium ion-permeable membrane comprising preferably crystalline beta-alumina as already described.

A schematic representation of a cell unit is shown in FIG. 6. In operation, electrons flow through the metal separator sheet 1 entering the molten sodium-containing cavity 2, wherein sodium cations combine with the electrons and are reduced to elemental sodium that is withdrawn from the cavity via line 3. The beta-alumina membrane 4 acts both as a physical separator and alkali ion conductor between the two cavities. Sodium polysulfide is introduced into cavity 5 via line 6;

it is, by its nature, highly ionized into sodium cations and polysulfide anions. The latter are oxidized to elemental sulfur that react further to yield sulfur-enriched polysulfide anions. The anions along with the requisite sodium cations are subsequently removed via line 7 from cavity 5 as sulfur-enriched sodium polysulfide (Na_2S_z where z varies from about 4.5 to 5.0). Electrons which are given up by the polysulfide anions flow through the metal separating sheet 8 to form a complete circuit. Thus the anode for one cell becomes the cathode for the next. The cell anode will comprise a porous or nonporous electron-conducting current collector such as graphite, molybdenum, titanium, chromium, aluminum, nickel-iron alloys and other alloys and the like.

As noted above, although beta-alumina is shown as the preferred separator, any other separator that is sufficient for the purposes may be employed. Additionally, an alternate embodiment comprises forming and continually removing elemental sulfur from the cell. In practice, the electrolytic cell 56 comprises a plurality of individual cell units in order to provide a sufficient output of sodium.

About 100–200 cells are operated in series in order to build up the overall voltage to about 300–600 volts. The total amount of cell area required depends on the amount of sodium required, and is in the range of 10 to 50 square feet per pound per minute of sodium. The temperature in the cell rises to about 700°–820°F., depending on the amount of cell area, current density used, the resistance of the cell elements and their condition.

The composition of the sodium polysulfide leaving to electrolytic cell can be controlled by the flow rate and the current. The greater the flow rate, the less is the increase in sulfur content; the greater the current, the greater is the increase in sulfur content. The composition is controlled such that by applying a reasonable vacuum (and/or heat if desired), sulfur corresponding to that which was removed from the oil can be taken overhead.

Accordingly, the sodium polysulfide formed in the electrolytic cell is passed via line 57 to surge vessel 58 and then to sulfur-reducing vessel 60 which is partially evacuated, e.g., to an absolute pressure of about 10 to about 300 mm Hg, preferably about 50 to 100 mm Hg, to vaporize some of the sulfur and reduce the sulfur content of the polysulfide so that the final polysulfide composition is Na_2S_x wherein x takes values ranging from about 4.0 to about 4.9, preferably about 4.4 to about 4.8. At one-tenth atmosphere sulfur vapor pressure, for example, the composition in equilibrium therewith is approximately $\text{Na}_2\text{S}_{4.82}$ at 700°F., $\text{Na}_2\text{S}_{4.73}$ at 750°F. and $\text{Na}_2\text{S}_{4.64}$ at 800°F. The sulfur vapor is taken overhead through line 61 and condensed by conventional means (not shown). As indicated supra the resulting polysulfide is then recycled via line 49 to scrubbing tower 48. Alternatively, at least a portion of the sodium polysulfide stream exiting from the cell can be contacted directly with the H_2S -treated salt mixture, thereby by-passing the evacuating operation in vessel 60. Thus, for example Na_2S_5 exiting from the cell can be contacted directly with the H_2S -treated salt mixture. The molten sodium is subsequently removed from the electrolytic cell and passed via line 62 to surge vessel 63 where it is blended with makeup sodium entering at line 64 and then fed via line 65, pump 66 and line 67 to vessel 11.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention will be more clearly understood by reference to the following examples:

Description of Apparatus and Procedures

A. Sodium Treatment Reaction

The reactor consisted of a standard, one liter Paar autoclave, which was constructed of Monel steel. Two modifications were made, however. An oversized turbine blade stirrer head was substituted for the standard item to aid in lifting and dispersing sodium and its alloys, particularly the alloy with lead. Also, the dipleg was fitted with a 50 micron metallic filter element to aid in sampling the oil phase when mixtures of salts and oil were present. The reactor head contained the usual openings and fittings for measurement of pressure and temperature and for the addition of gases.

In the typical run the reactor was charged at room temperature with the desired quantity of sulfur-containing oil and freshly cut sodium. Alternatively, in some runs, sodium was added as an alloy with lead. The reactor was sealed and thoroughly flushed with H_2 . About 50 psig of the H_2 was present when heatup was begun. The reactor temperature was brought to approximately 450°F. prior to beginning stirred contact, and the H_2 pressure increased to the desired run value, thereby minimizing the reaction time below the normal run temperature range of 600°–700°F.

The yield of gaseous products, comprising materials lighter than or the same weight as pentane was determined by cooling the reactor to room temperature, venting the gases through a wet test flow meter to determine volume and then submitting a representative sample for component analysis by mass spectrometry.

Coke formed in the desulfurization reaction was most often recovered with the sodium salts and is reported as the water-insoluble fraction of the salt.

Without exception, the combined coke and C_5^- gas yield never amounted to more than 1.0 wt. percent of the feed and usually was less than 0.5 wt. percent on feed. Therefore, coke and gas yields are not reported in the examples which follow. Also, desulfurized oil recoveries were essentially quantitative in all examples.

B. Hydrogen Sulfide or Water Treatment Preparatory to Salt Recovery

The reagent of choice, water or hydrogen sulfide, was added directly to the reactor mixture contained in the sodium treating reactor. Normally, the addition was made immediately at the end of the sodium treating step and at the same temperature employed in the sodium treating step. A weighed amount of reagent was loaded into a 200 ml. stainless steel bomb which was then fitted to a reactor inlet valve. In the case of water, either hydrogen or nitrogen pressure was used to force the bomb contents into the reactor. Hydrogen sulfide was injected under its own vapor pressure. The bomb, previously tared, was always reweighed after addition to determine the amount of reagent retained.

C. Separation of the Oil and Salt Phases

Again, the sodium treating reactor was used. After injection of water or hydrogen sulfide, stirring was ceased for a time period sufficient to allow the salt phase, either macrocrystalline solids or molten salts, to settle (salts exhibit density roughly twice that of oil). If desired, oil samples could then be withdrawn through the filter-modified dipleg, while still at the approximate temperature of the sodium-treating reaction. Ulti-

mately, however, the reactor was cooled to ~200°F., opened, and the bulk of the oil phase decanted. Precipitated salts were slurry washed with toluene to remove adhering oil and then dried. If the preparatory treatment was designed for generation of molten salts then the reactor was cooled to 200°F. without agitation. In this case the salts formed a solid layer on the reactor bottoms and were removed with hammer and chisel. The solidified molten layer was subsequently crushed, hydrocarbon washed and dried.

As an alternative salt recovery technique to that of water treatment, salt removal could be effectuated by treatment of same with acetic acid. In this process, the reaction mixture at the end of the sodium-treating step was cooled to 180°F., diluted with 300 volume percent of toluene and then treated with 130 mole percent acetic acid based on moles (atoms) of sodium present. Acid addition was made slowly with stirring to avoid excessive frothing. The mixture was heated on a steam bath for 1 hour with a nitrogen purge and then filtered to recover a salt-free product. The toluene diluent and excess acetic acid were removed by distillation prior to analyzing the desulfurized oil.

The acetic acid treatment converts a large portion of the salts present in the oil to sodium acetate which is readily recovered by filtration. The sodium sulfide compound reacts to give H_2S which is removed in the nitrogen stripping operation.

D. Salt Analyses

1. The total analysis of the sodium sulfide salt mixtures was based on the procedure outlined in Scott's Standard Methods of Chemical Analysis, Fifth Edition, (1939), Volume 2, pp. 2181–2187.

2. The procedure for determining the hydrocarbon insoluble sludge content of the reactor mixture required cooling of same to 180°F. and dilution with 300 volume percent toluene. The diluted mixture was then simply filtered under a nitrogen atmosphere to recover the sludge. Caution should be used in that the sludge is pyrophoric. The sludge was washed free of adhering oil and inorganic salts with toluene and was dried under vacuum.

E. Oil Product Analyses

Sodium-treated oil products were analyzed not only for sulfur content, but also for changes in metals content and general physical properties such as API gravity, viscosity and asphaltene content. The oil product obtained from each recovery scheme was filtered hot through a number 2 grade Whatman paper prior to analysis. In the case of the water-treated salts, a sample of the filtered oil was always refluxed in toluene with a small amount of acetic acid to decompose any salts that escaped filtration and particularly oil soluble salts such as the sodium mercaptides. The salt product from this step was sodium acetate which was filtered from the solution. Finally, desulfurized oil was recovered by distillation to remove toluene diluent.

F. Sulfur-Containing Feedstocks

This invention has been demonstrated with several different sulfur-containing feedstocks. These include both the 650+°F. and 1,030+°F. fractions of the Ba-chequero and Tia Juana crudes from South America and also the Kuwait and Safaniya crudes from the Middle East. Examples hereinbelow, however, are based on the 650°F+ Safaniya and Tia Juana fractions, which are considered to be typical of the residuum feeds to be encountered commercially. The properties of these feeds are noted below.

FEEDSTOCK INSPECTIONS

Feed Designation	Safaniya	Tia Juana
API Gravity	14.4	15.0
Sulfur, Wt. %	3.91	2.2
Nitrogen, Wt. %	0.26	0.35
Carbon Wt. %	84.42	86.19
Hydrogen, Wt. %	11.14	11.38
Oxygen, Wt. %	0.27	0.30
Conradson Carbon, Wt. %	11.82	11.60
Metals, ppm		
Ni	20	34
V	77	273
Fe	4	—
Viscosity		
VSF at 122°F.	235	373
140°F.	131	193
Pour Point, ° F.	33	35
Naphtha Insolubles, Wt. %	7	7.5
R.I. at 67°C.		
Flash Point, °F.	318	315

EXAMPLE 1

The data shown below in Table I demonstrate the effect of hydrogen on the amount of sludge formed during the de-sulfurization reaction.

TABLE I
SODIUM DESULFURIZATION WITH HYDROGEN ADDITION¹

Run No.	1	2
Hydrogen added	No	Yes
Hydrogen used, SCF/B	0	130 ²
Contact time, Hr.	1.5	1.5
Desulfurization, Wt. %	92.7	92.4
Selectivity, Wt. % ³	68	80.0
Wt. % Insol. Sludge in Reaction Mix	16.7	1.6
Finished Oil Viscosity SFS at 122°F.	230	65

¹ Data obtained from Na/Pb alloy (containing 10 wt. % Na) desulfurization of Safaniya atmospheric residuum (containing 3.9 wt. % sulfur), at a temperature of 650°F.

² 150 psig hydrogen

³ Percent of reacted sodium found as Na₂S

It is seen that the amount of sludge formed in the reaction is decreased dramatically when low pressure hydrogen is present; moreover, the overall oil viscosity is substantially reduced and the selectivity substantially increased.

EXAMPLE 2

Additional data is tabularized below in Table II, demonstrating the increased product quality and selectivity when low pressure hydrogen is used in the desulfurization reaction.

TABLE II.—THE EFFECT OF HYDROGEN ON DESULFURIZATION OF RESIDUA WITH SODIUM

(Batch tests at 650° F. for 1 hr. contact)

Run number	1	2	3	4	5	6
Resid source	Safaniya	Safaniya	Safaniya	Safaniya	Tia Juana	Tia Juana
Reactants:						
Resid, g.	335	317.2	489.6	492	417.0	411.
Sodium, g.	25.6 ¹	20.3 ¹	36.2	34.3	16.6	16.2
Hydrogen, p.s.i. at run temp.	0	180	0	200	0	200
Resid-salt	Acetic acid ²	Acetic acid ²	H ₂ O ³	H ₂ O ³	H ₂ O ³	H ₂ O ³
Separation method	Decomposition	Decomposition	Precip.	Precip.	Precip.	Precip.
Resid product analyses:						
Sulfur, weight percent	0.28	0.30	0.4	0.28	0.59	0.37
Asphaltenes, weight percent	14+	6	21	7		
Naphtha insol. weight percent					15	8
Conradson carbon, weight percent			13	11		
Metals, Ni/V/Fe, p.p.m.			40/60/53	16/30/4	103/245/39	26/119/11
Viscosity, SFS at 122° F	230	65	181	81		196
API gravity			17	22		
Desulfurization, percent	92.7	92.4	89.7	92.8	73.2	83.2
Selectivity, percent ⁴	68	80	68	75	57.8	67.0

¹ Sodium added as alloy with lead. A 10% Na-90% Pb alloy.

² Acetic acid converts sulfide salt to sodium acetate and H₂S.

³ Added about 50 mole percent H₂O on total salts at 650° F. to agglomerate salts. Recovered oil by filtration.

⁴ Percent of reacted sodium found as Na₂S.

As can be seen, product quality along with selectivity is improved using hydrogen. Moreover, the presence of hydrogen surprisingly aids in demetallization of the oil. The unexpected demetallization activity does not occur when hydrogen is present alone so that the presence of both sodium and hydrogen is required. Additionally, it is seen that less sodium is required in the presence of hydrogen to obtain a high level of desulfurization than in the absence of hydrogen (compare runs 1 and 2).

EXAMPLE 3

This example shows the effect of hydrogen pressure on process efficiency.

TABLE III
THE EFFECT OF HYDROGEN PRESSURE
(Batch Tests at 650°F. for 1 Hr. with Safaniya Atmospheric Resid)

Run No.	1	2	3	4
Reactants				
Resid, g.	402	492	403	489.6
Sodium, g.	25	34.3	25	36.2
Hydrogen, psig at run temp.	50	200	500	0
Resid-Salt Separation Method	H ₂ O ⁽¹⁾ percip.	H ₂ O ⁽¹⁾ percip.	H ₂ O ⁽¹⁾ percip.	H ₂ O ⁽¹⁾ percip.
Resid Product Analyses				
Sulfur, Wt. %	0.54	0.28	0.45	0.4
Asphaltenes, Wt. %	8.2	7	—	21
Metals, Ni/V/Fe, ppm	15/50/14	16/30/4	16/30/10	40/60/53
Viscosity, SFS at 122°F.	—	81	—	181
API Gravity	19.6	22	—	17
Desulfurization, %	86.3	92.8	88.4	89.7
Selectivity, % ⁽²⁾	78.3	75	80.5	68

¹ Added about 50 mole % H₂O on total salts at 650°F. Recovered agglomerated salts by filtrations.

² Percent of reacted sodium found as Na₂S

Comparing runs 1-3, it is seen that hydrogen pressures as low as 50 psig can be effectively used in the process. Moreover, good demetallization activity is observed when hydrogen is present.

1. A process for the desulfurization of a sulfur and metals-containing petroleum oil stock comprising contacting said oil stock in a desulfurization zone with a desulfurization agent selected from the group consisting of the alkali metals and alloys thereof, and a hydrogen-containing stream, at desulfurization conditions, thereby forming a mixture comprising oil of reduced sulfur and metals content containing alkali metal salts and contacting at least a portion of said mixture with water at a temperature above about 500°F.

2. The process of claim 1 wherein the hydrogen pressure in said desulfurization zone ranges between about 25 and about 800 psig.

3. The process of claim 2 wherein said hydrogen pressure ranges between about 100 and 200 psig.

4. The process of claim 1 wherein said alkali metal is sodium and said alkali metal alloy is a mixture of sodium and lead.

5. The process of claim 20 wherein said mixture is contacted with about 10 to about 400 mole percent H_2S , based on total moles of salt present in said mixture.

6. The process of claim 5 wherein about 30 to about 60 mole % H_2S , based on total moles of salt present in said mixture, is contacted with said mixture.

7. The process of claim 5 wherein about 120 to about 160 mole % H_2S , based on total moles of salt present in said mixture, is contacted with said mixture.

8. The process of claim 7 wherein the H_2S -treated mixture comprises a salt phase and an oil phase and where said salt phase is substantially separated from said oil phase and at least a portion of said salt phase contacted with molten sulfur.

9. The process of claim 1 wherein said water is contacted with said mixture in amounts ranging between about 10 and about 80 mole percent, based on total number of moles of salt present in the mixture.

10. The process of claim 1 wherein said water is contacted with said mixture in an amount ranging between about 110 and 200 mole percent, based on total number of moles of salt present in the mixture, and, thereafter, cooling the water-treated mixture to a temperature below about 250°F. thereby agglomerating the salts.

11. A process for the desulfurization of a sulfur-containing petroleum oil stock comprising contacting said oil stock, in a desulfurization zone, with a desulfurization agent selected from the group consisting of sodium and alloys thereof, in the presence of a hydrogen-containing stream thereby forming a mixture comprising oil containing sodium metal salts dispersed therein, contacting at least a portion of said mixture with water or H_2S , thereby forming a mixture comprising an oil phase of reduced sulfur content and a salt phase, con-

tacting at least a portion of said phase with a sulfur-rich sodium polysulfide, thereby forming a mixture comprising a sulfur-depleted sodium polysulfide and, thereafter, using at least a portion of said sulfur-depleted sodium polysulfide as an electrolyte in an electrolytic cell for the production of sodium metal.

12. The process of claim 11 wherein the hydrogen pressure ranges between about 25 to 800 psig.

13. The process of claim 11 wherein said sulfur-rich sodium polysulfide is Na_2S_5 .

14. The process of claim 11 wherein said sulfur-rich sodium polysulfide is represented by the formula Na_2S_x , where x takes values ranging between about 4.0 and about 4.9 and said sulfur-depleted sodium polysulfide is represented by the formula Na_2S_y , where y takes values ranging between about 2.8 and 4.5.

15. The process of claim 11 wherein the oil containing sodium metal salts dispersed therein is contacted with water.

16. The process of claim 15 wherein the sulfur-depleted sodium polysulfide-containing mixture also contains NaOH and is treated with about 0.5 to about 1.0 moles of H_2S , based on moles of NaOH present in the mixture.

17. The process of claim 11 wherein said electrolytic cell comprises an anodic cavity containing polysulfide anions and a cathodic cavity containing sodium metal, said anodic and cathodic cavities separated by means of a sodium-ion-conducting membrane comprising beta-alumina.

18. A process for the desulfurization of a sulfur and metals-containing petroleum oil stock comprising contacting said petroleum oil stock, in a desulfurization zone, with a desulfurization agent selected from the group consisting of the alkali metals and alloys thereof, and a hydrogen-containing stream, thereby forming a mixture comprising oil of reduced sulfur and metals content containing alkali metal salts and contacting at least a portion of said mixture with H_2S .

19. The process of claim 18 wherein the hydrogen partial pressure in said desulfurization zone ranges between about 25 and 500 psig.

* * * * *

45

50

55

60

65