Petroleum & Minerals Engineering
Petroleum Process Engineering Dep.
3rd stage
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Petroleum Refinery

PRODUCT TREATING

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Product Treatment

Fractions or streams produced by crude distillation, cracking, and other refinery processes often contain small amounts of impurities that must be removed. Processes that remove these undesirable components are known as treating processes, and these processes are used not only to finish products for the market but also to prepare feedstocks for other processes (catalytic polymerization and reforming) in which catalysts would be harmed by impurities .

Treating in a petroleum refinery is a means by which contaminants such as organic compounds containing sulfur, nitrogen, oxygen, dissolved metals, inorganic salts & soluble salts dissolved in emulsified water are removed from petroleum fractions or streams .

Petroleum refinery has a choice of several different treating processes, but the primary purpose of the majority of them is the elimination of unwanted sulfur compounds .

A variety of intermediate & finished products include middle distillates , Gasoline, Kerosene, Jet fuel & sulfur gases are dried & sweetened.

A major refinery treatment of gasoline treats sulfur compounds (Hydrogen sulfides , Thiophenes, disulfides & Mercaptan) to improve color, odor & oxidation stability. Sweetening also reduces concentration of carbon dioxides.

Choices of a treatment method depend on the amount and type of impurities in the fractions to be treated and the extent to which the process removes the impurities.

Some processes are limited to the conversion of certain sulfur compounds, as well as olefins, asphaltic materials, oxygen compounds, and nitrogen compounds. The various processes eliminate impurities by chemical reagents, by catalysts, and by adsorption on clays or similar materials.

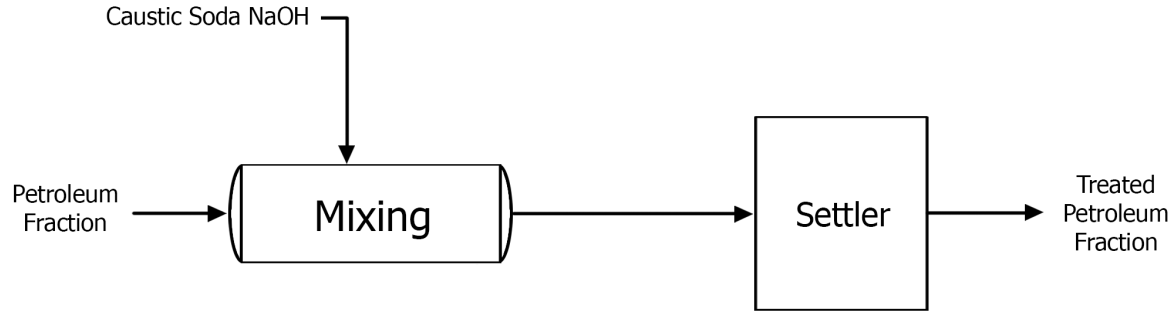
Caustic sweetinig process produce organic by product ((Phenolic caustic & naphthenic caustic solutions)) that must be accounted for When designing a treating plant is the most widely used alternative to caustic sweetinig & is very effective.

تصغر العقول عندما تنشغل بعقول الآخرين ،
وتكبر العقول عندما تركز على ذاتها !!

CAUSTIC PROCESSES :

Treating of petroleum products by washing with solutions of alkali (caustic or lye) is almost as old as the petroleum industry itself. Early discoveries that product odor and color could be improved by removing organic acids (naphthenic acids and phenols) and sulfur compounds (mercaptans and hydrogen sulfide) led to the development of caustic washing.

Thus, it is not surprising that caustic soda washing (lye treatment) has been used widely on many petroleum fractions. In fact, it is sometimes used as a pretreatment for sweetening and other processes. The process consists of mixing a water solution of lye (sodium hydroxide or caustic soda) with a petroleum fraction. The treatment is carried out as soon as possible after the petroleum fraction is distilled, as contact with air forms free sulfur, which is very corrosive and difficult to remove. The lye reacts with any hydrogen sulfide present to form sodium sulfide, which is soluble in water.



Caustic Processes

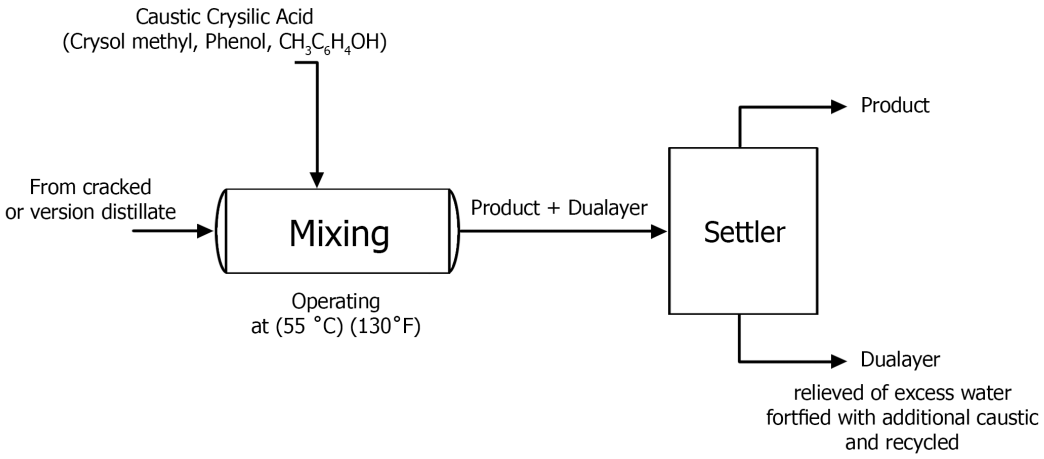
* Used for petroleum products

Dualayer Distillate Process :

The Dualayer distillate process is similar in character to the Duosol process in that it uses caustic solution and cresylic acid (cresol, methylphenol, $CH_3.C_6H_4.OH$). The process extracts organic acid substances (including mercaptans, R–SH) from cracked, or virgin, distillate fuels.

In a typical operation, the Dualayer reagent is mixed with the distillate at about 55ºC (130ºF) and passed to the settler, where three layers separate with the aid of electrical coagulation.

The product is withdrawn from the top layer; the Dualayer reagent is withdrawn from the bottom layer, relieved of excess water, fortified with additional caustic, and recycled.



Dualayer Distillation Process

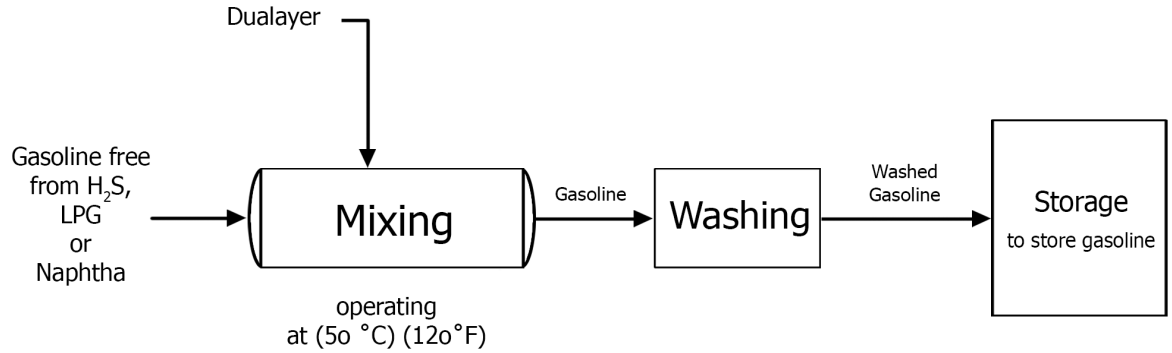
* Used for cracked or version distillate fuel

Dualayer Gasoline Process :

The Dualayer gasoline process is a modification of the Dualayer distillate process in that it is used to extract mercaptans from liquid petroleum gas, gasoline, and naphtha using the Dualayer reagents.

Thus gasoline, free of hydrogen sulfide, is contacted with the Dualayer solution at 50ºC (120ºF) in at least two stages, after which the treated gasoline is washed and stored.

The treating solution is diluted with water (60% to 70% of the solution volume) and stripped of mercaptans, gasoline, and excess water, and the correct amount of fresh caustic is added to obtain the regenerated reagent.



Dualayer Gasoline Process

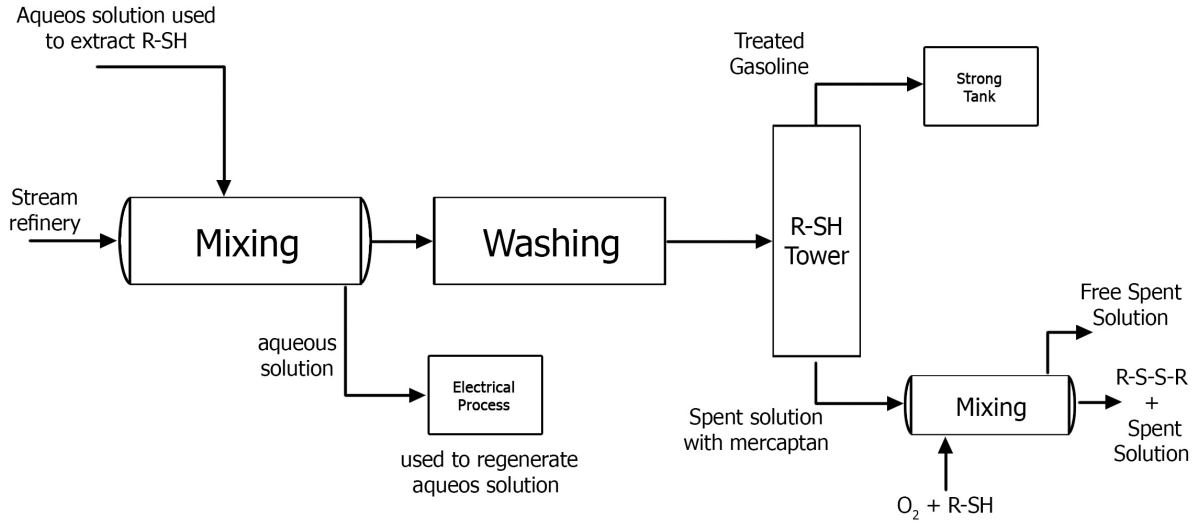
* Used for : Gasoline , LPG & Naphtha

Electrolytic Mercaptan Process:

The electrolytic mercaptan process employs aqueous solutions to extract mercaptans from refinery streams, and the electrolytic process is used to regenerate the solution.

The charge stock is pre-washed to remove hydrogen sulfide and contacted countercurrently with the treating solution in a mercaptan extraction tower.

The treated gasoline is stored; the spent solution is mixed with regenerated solution and oxygen. The mixture is pumped to the cell, where mercaptans are converted to disulfides that are separated from the regenerated solution.



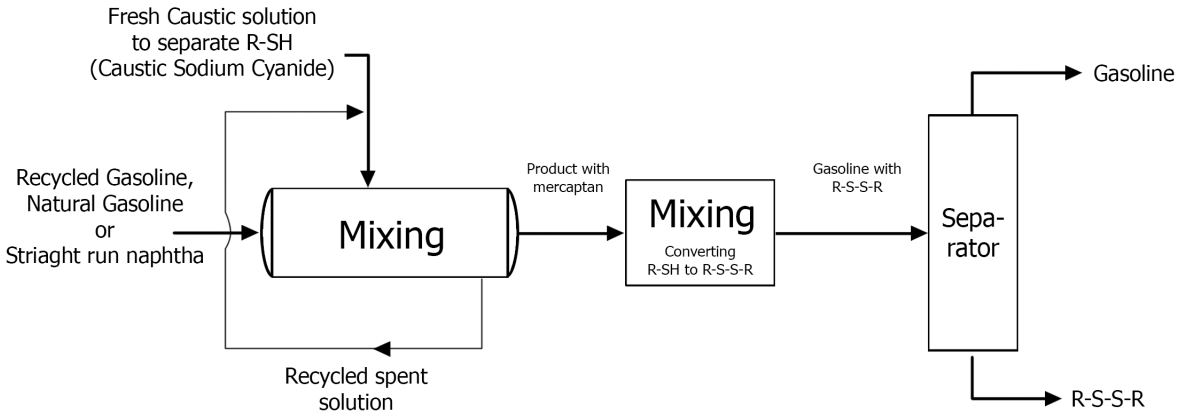
Electrolytic mercaptans process

*General method used for all products

Ferrocyanide Process :

The ferrocyanide process is a regenerative chemical treatment for removing mercaptans from straight-run naphtha, as well as natural and recycle gasoline, using caustic-sodium ferrocyanide reagent.

For example, gasoline is washed with caustic to remove hydrogen sulfide and then washed countercurrently in a tower with the treating agent. The spent solution is mixed with fresh solution containing ferricyanide; the mercaptans are converted to insoluble disulfides and are removed by a countercurrent hydrocarbon wash. The solution is then recycled, and part of the ferrocyanide is converted to ferricyanide by an electrolyzer.



Ferrocyanide Process

* Used for : Recycled gasoline , Natural gasoline ,& Striaght run naphtha

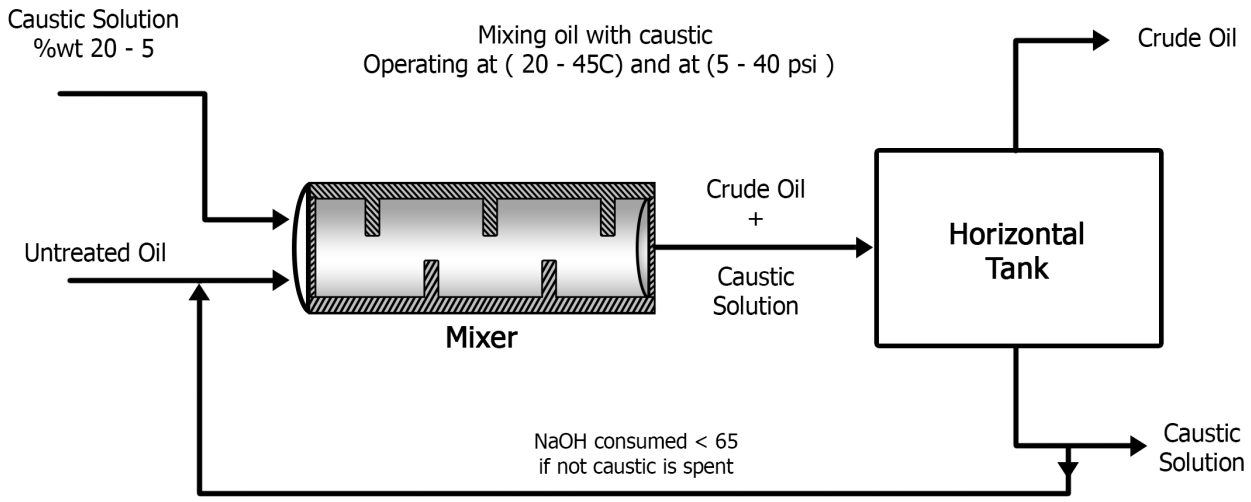
Lye Treatment :

Lye treatment is carried out in continuous treaters, which essentially consist of a pipe containing baffles or other mixing devices into which the oil and lye solution are both pumped. The pipe discharges into a horizontal tank where the lye solution and oil separate. Treated oil is withdrawn from near the top of the tank; lye solution is withdrawn from the bottom and recirculated to mix with incoming untreated oil. A lye-treating unit may be incorporated as part of a processing unit, for example, the overhead from a bubble tower may be condensed,

cooled, and passed immediately through a lye-treating unit. Such a unit is often referred to as a worm-end treater, as the unit is attached to the particular unit as a point beyond the cooling coil or cooling worm.

Caustic solutions ranging from 5% to 20% wt% are used at 20˚C to 45˚C (70˚F to 110˚F) and 5 to 40 psi. High temperatures and strong caustic are usually avoided because of the risk of color body formation and stability loss. Caustic-product treatment ratios vary from 1:1 to 1:10.

Spent lye is the term given to a lye solution in which about 65% of the sodium hydroxide content has been used by reaction with hydrogen sulfide, light mercaptans, organic acids, or mineral acids. A lye solution that is spent, as far as hydrogen sulfide is concerned, may still be used to remove mineral or organic acids from petroleum fractions. Lye solution spent by hydrogen sulfide is not regenerated, whereas blowing with steam can regenerate lye solution spent by mercaptans. This technique reforms sodium hydroxide and mercaptans from the spent lye. The mercaptans separate as a vapor and are normally destroyed by burning in a furnace. Spent lye can also be regenerated in a stripper tower with steam, and the overhead consists of steam and mercaptans, as well as the small amount of oil picked up by the lye solution during treatment. Condensing the overhead allows the mercaptans to separate from the water.

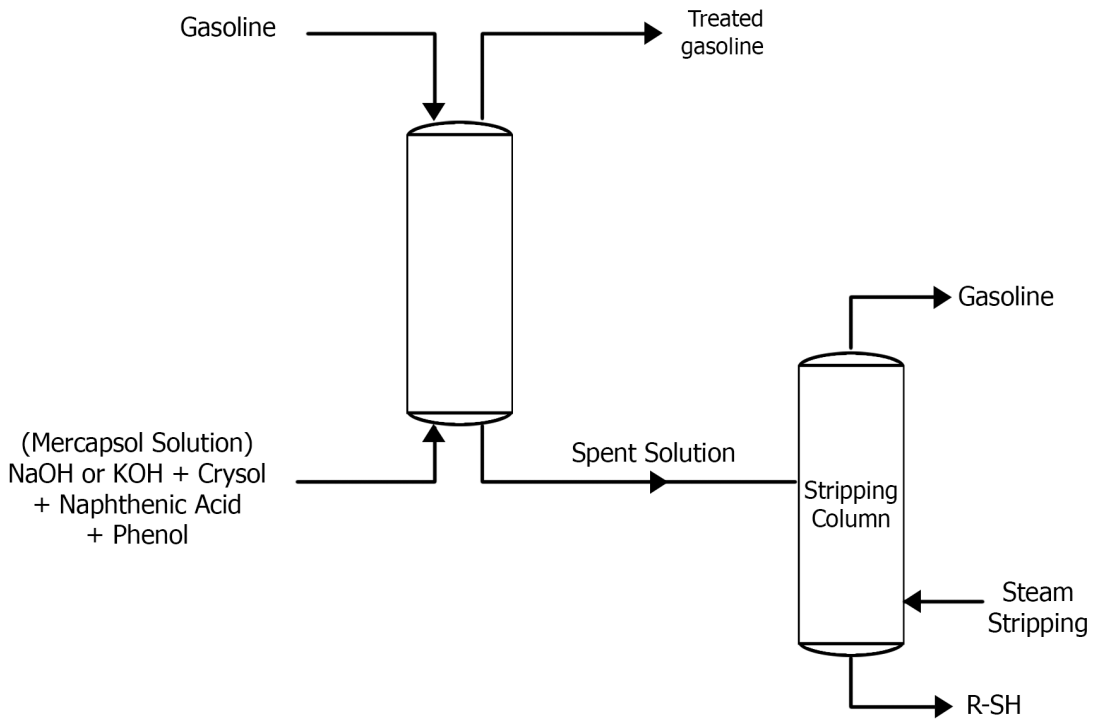


Lye Treatment

*Used for crude oil

Mercapsol Process :

The Mercapsol process is another regenerative process for extracting mercaptans by means of sodium (or potassium) hydroxide, together with cresols, naphthenic acids, and phenol. Gasoline is contacted countercurrently with the Mercapsol solution, and the treated product is removed from the top of the tower. Spent solution is stripped to remove gasoline, and the mercaptans are then removed by steam stripping.



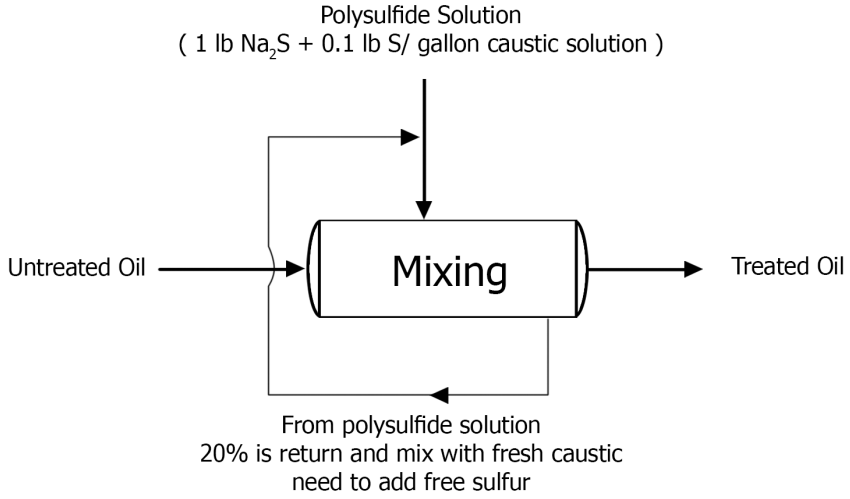
Mercapsol Process

* Used for Gasoline

Polysulfide Treatment

Polysulfide treatment is a non-regenerative chemical treatment process used to remove elemental sulfur from refinery liquids. Dissolving 1 Lb of sodium sulfide (Na_2S) and 0.1 Lb of elemental sulfur in a gallon of caustic solution prepare the polysulfide solution. The sodium sulfide can actually be prepared in the refinery by passing hydrogen sulfide, an obnoxious refinery by-product gas, through a caustic solution.

The solution is most active when the composition approximates Na_2S to Na_2S_3 but activity decreases rapidly when the composition approaches Na_2S_4. When the solution is discarded, a portion (about 20%) is retained and mixed with fresh caustic-sulfide solution, which eliminates the need to add free sulfur. Indeed, if the material to be treated contains hydrogen sulfide in addition to free sulfur, it is often necessary to simply add fresh caustic.



Polysulfide Treatment

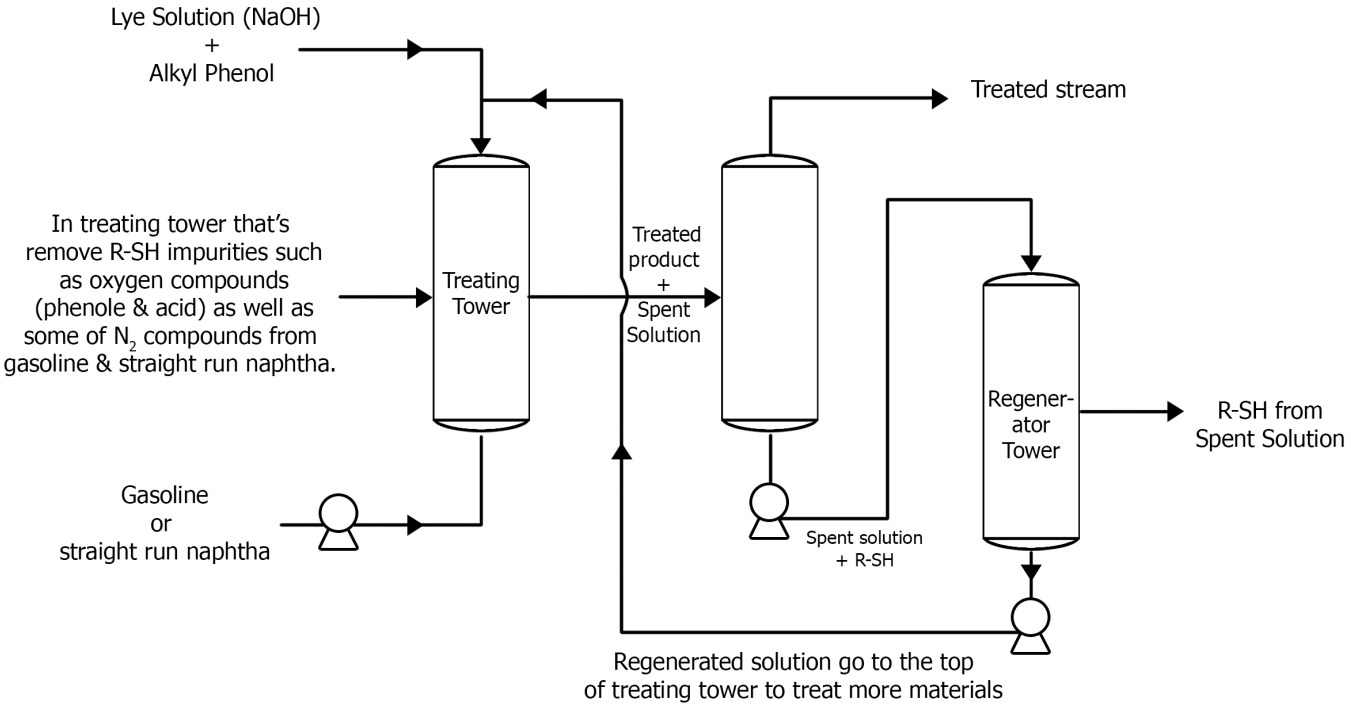
* For crude oil

Sodasol Process :

A lye solution removes only the lighter or lower-boiling mercaptans, but various chemicals can be added to the lye solution to increase its ability to dissolve the heavier mercaptans. The added chemicals are generally known as solubility promoters or solutizers. Several different solutizers have been patented and are used in processes that differ chiefly in the composition of the solutizers.

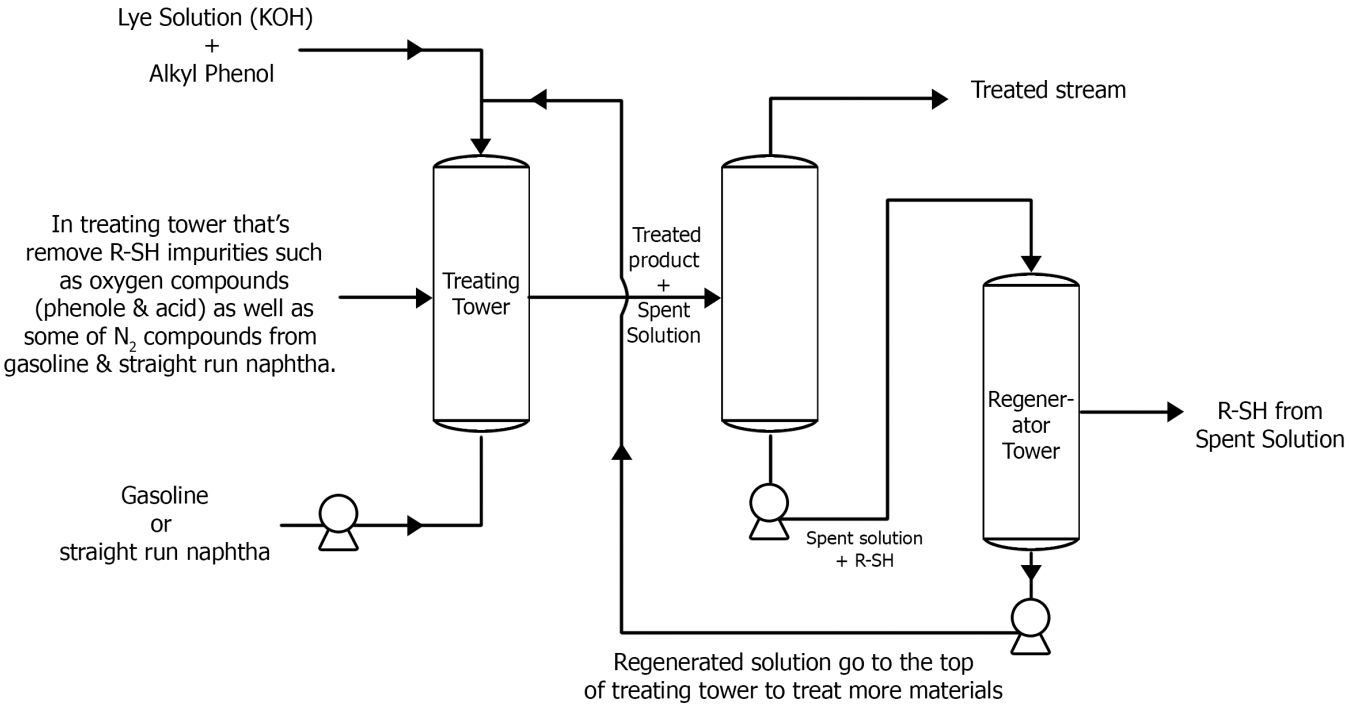
In the Sodasol process, the treating solution is composed of lye solution and alkyl phenols (acid oils), which occur in cracked naphtha and cracked gas oil and are obtained by washing cracked naphtha or cracked gas oil with the lye solution. The lye solution, with solutizers incorporated, is then ready to treat product streams, such as straight-run naphtha and gasoline. The process is carried out by pumping a sour stream up a treating tower counter- current to a stream of Sodasol solution that flows down the tower. As the two streams mix and pass, the solution removes mercaptans and other impurities, such as oxygen compounds (phenols and acids), as well as some nitrogen compounds.

The treated stream leaves the top of the tower; the spent Sodasol solution leaves the bottom of the tower to be pumped to the top of a regeneration tower, where mercaptans are removed from the solution by steam. The regenerated Sodasol solution is then pumped to the top of the treatment tower to treat more material. A variation of the Sodasol process is the Potasol process, which uses potassium hydroxide instead of lye (sodium hydroxide).



Sodasol Process

* Used for Gasoline & Straight run naphtha to remove R-SH and other impurities such as oxygen compounds (phenol & acids) as well as some nitrogen compounds



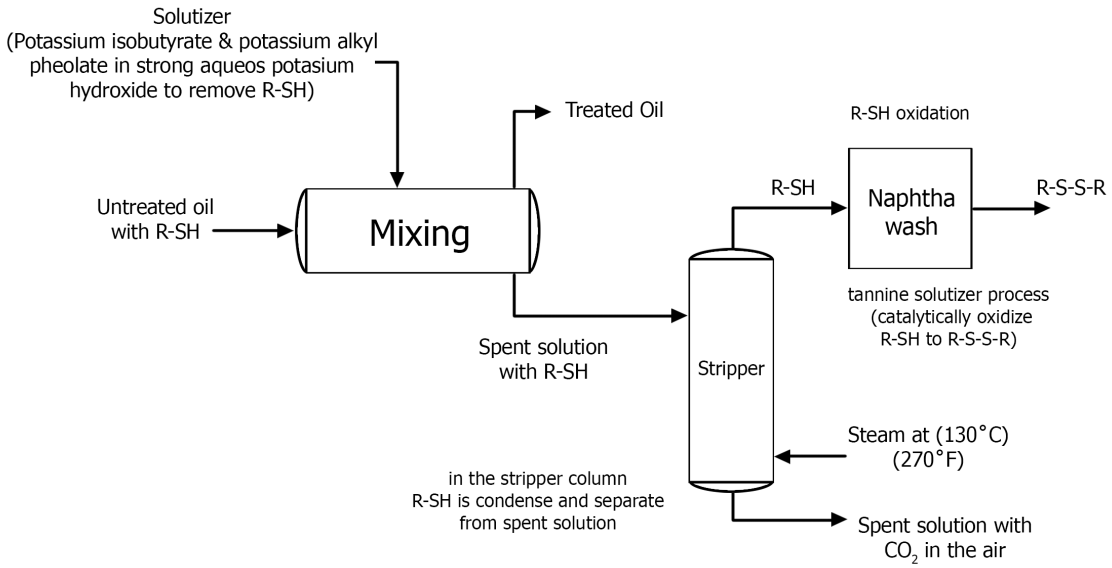
Potasol Process

* Used for Gasoline & Straight run naphtha to remove R-SH and other impurities such as oxygen compounds (phenol & acids) as well as some nitrogen compounds

Solutizer Process

The Solutizer process is a regenerative process that uses such materials as potassium iso- butyrate and potassium alkylphenolate in strong aqueous potassium hydroxide to remove mercaptans. After removal of the mercaptans and recovery of the hydrocarbon stream, regeneration of the spent solution may be achieved by heating and steam blowing at 130˚C (270˚F) in a stripping column in which steam and mercaptans are condensed and separated.

On the other hand, the spent solution may be contacted with carbon dioxide air, after which the disulfides formed by oxidation of the mercaptans are extracted by a naphtha wash. Air blowing in the presence of tannin (tannin Solutizer process) catalytically oxidizes mercaptans to the corresponding disulfides

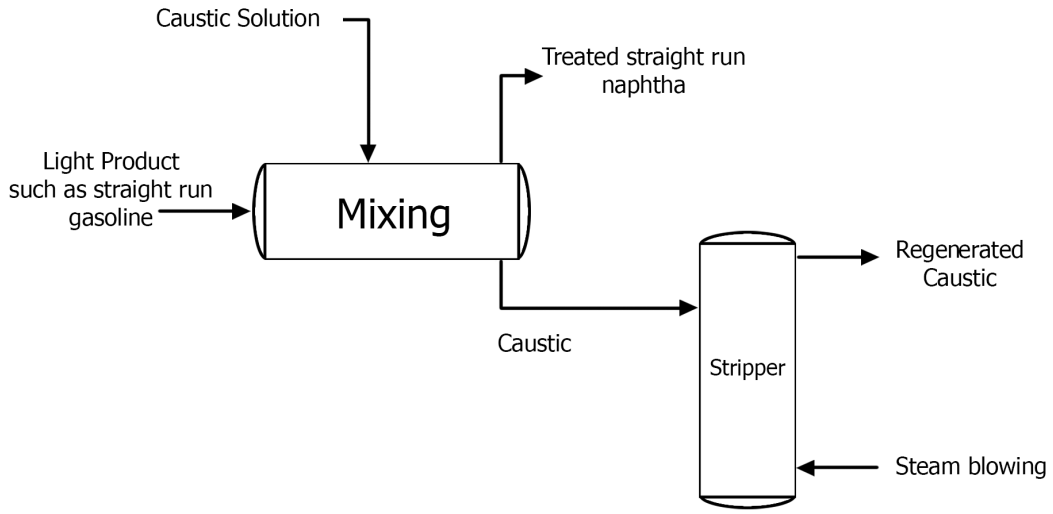


Solutizer Process

* Used to remove heavey and lower Mercaptan from products.

Steam-Regenerative Caustic Treatment :

Steam-regenerative caustic treatment is essentially directed toward removal of mercaptans from such products as light, straight-run gasoline. The caustic is regenerated by steam blowing in a stripping tower.

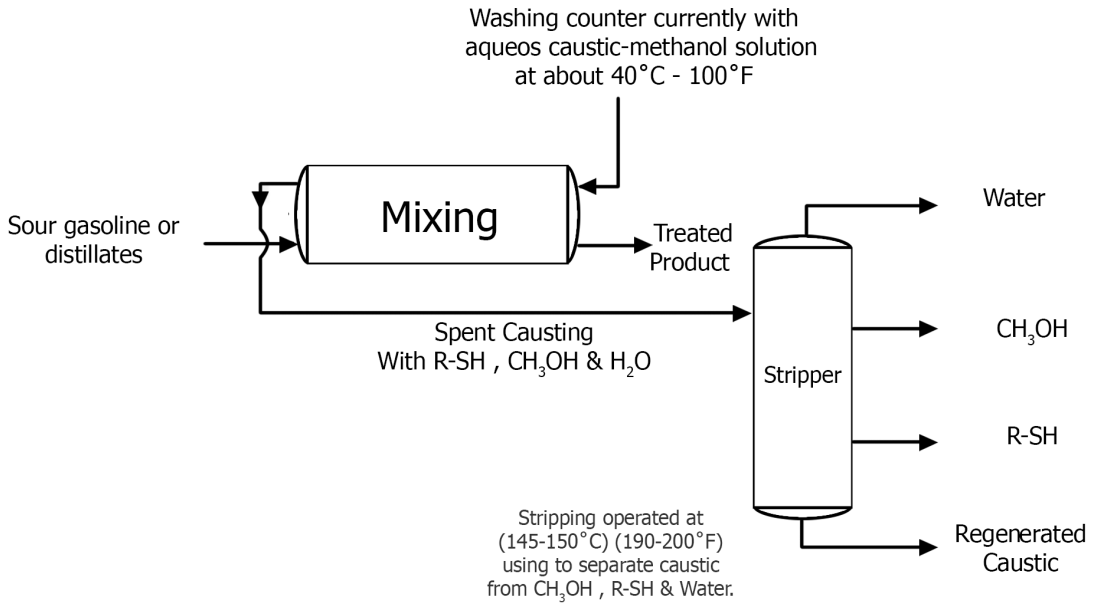


Steam Regeneration Caustic Treatment

* Used For products as light straight run gasoline

Unisol Process :

The Unisol process is a regenerative method for extracting not only mercaptans but also certain nitrogen compounds from sour gasoline or distillates. The gasoline, free of hydrogen sulfide, is washed countercurrently with aqueous caustic-methanol solution at about 40˚C (100˚F). The spent caustic is regenerated in a stripping tower (145˚C to 150˚C, 290˚F to 300˚F), where methanol, water, and mercaptans are removed.



Unisol Process

* Used For extracting mercaptan and certain nitrogen compounds from sour gasoline or distillates.