PETROLEUM: CHEMISTRY, REFINING, FUELS AND PETROCHEMICALS - PRODUCT TREATING

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Summary

Fractions or streams produced by crude distillation, cracking, and other refinery processes (although usable in the refinery as process feedstocks) 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 such as *polymerization* and *reforming*) in which catalysts would be harmed by impurities.

1. Introduction

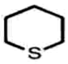
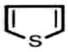
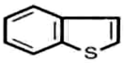
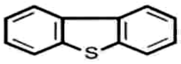
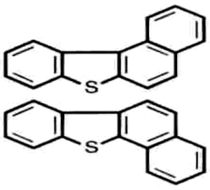
RSH	Thiols (Mercaptans)
RSR'	Sulfides
	Cyclic Sulfides
RSSR'	Disulfides
	Thiophene
	Benzothiophene
	Dibenzothiophene
	Naphthobenzothiophene

Table 1. Sulfur types in crude oil.

Treating in petroleum refining is a means by which contaminants such as organic compounds containing sulfur (Table 1), nitrogen (Table 2), and oxygen; dissolved metals and inorganic salts; and soluble salts dissolved in emulsified water are removed from petroleum fractions or streams. Petroleum refiners have 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 and finished products, including middle distillates, gasoline, kerosene, jet fuel, and sour gases are dried and sweetened. Sweetening, a major refinery treatment of gasoline, treats sulfur compounds (hydrogen sulfide, thiophene and mercaptan) to improve color, odor, and oxidation stability. Sweetening also reduces concentrations of carbon dioxide.

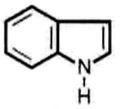
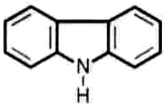
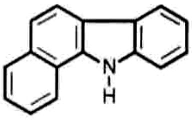
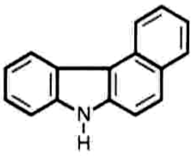
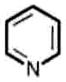
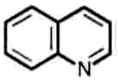
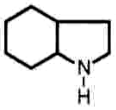
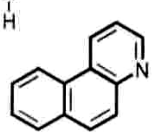
Nonbasic		
Pyrrole	C_4H_5N	
Indole	C_8H_7N	
Carbazole	$C_{12}H_9N$	
Benzo(a)carbazole	$C_{16}H_{11}N$	 
Basic		
Pyridine	C_5H_5N	
Quinoline	C_9H_7N	
Indoline	C_8H_9N	
Benzo(f)quinoline	$C_{13}H_9N$	

Table 2. Nitrogen types in crude oil.

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. Naturally occurring sweet kerosene, for example, may require only a simple treatment with alkali (*lye*) to remove hydrogen sulfide. If mercaptans are also present in the raw kerosene, a doctor treatment in addition to *lye treatment* is required, but poor-quality raw kerosene may require, in addition to these treatments, treatment with sulfuric acid and fuller's earth. The lowest quality raw kerosene requires treatment with strong sulfuric acid, neutralization with lye, and redistillation. Since different fractions have the same impurities, the same treatment process may be used for several different products.

Caustic sweetening processes produce organic byproducts (phenolic caustic and naphthenic caustic solutions) that must be accounted for when designing a treating plant. Hydrotreating (Section 6.186R) is the most widely used alternative to caustic sweetening and is very effective.

2. 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.

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, since 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:

2.1. 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, $CH_3C_6H_4OH$). 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 55°C (130°F) 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.

2.2. 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 50°C (120°F) 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.

2.3. 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 counter currently 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.

2.4. 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 counter currently 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.

2.5. 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*, since 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% w/w are used at 20 to 45°C (70 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.

Non-regenerative caustic treatment is generally economically applied when the contaminating materials are low in concentration and waste disposal is not a problem. However, the use of non-regenerative systems is on the decline because of the frequently occurring waste disposal problems that arise from environmental considerations and because of the availability of numerous other processes that can effect more complete removal of contaminating materials.

2.6. 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 counter currently 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.

2.7. Polysulfide Treatment

Polysulfide treatment is a non-regenerative chemical treatment process used to remove elemental sulfur from refinery liquids. Dissolving 1 pound of sodium sulfide (Na_2S) and 0.1 pound 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 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 (ca. 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 simply to add fresh caustic.

2.8. 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 countercurrent 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).

2.9. Solutizer Process

The *Solutizer process* is a regenerative process using 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, but there may be side reactions that can lead to reagent contamination.

2.10. Steam Regenerative Caustic Treatment

Steam-regenerative caustic treatment is essentially directed towards removal of mercaptans from such products as light, straight-run gasoline. The caustic is regenerated by steam blowing in a stripping tower. The nature and concentration of the mercaptans to be removed dictate the quantity and temperature of the process. However, the caustic solution gradually deteriorates because of the accumulation of material that cannot be removed by stripping; the caustic quality must be maintained by either continuous or intermittent discarding or replacement, of a minimum amount of the operating solution.

2.11. 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 counter currently with aqueous caustic-methanol solution at about 40°C (100°F). The spent caustic is regenerated in a stripping tower (145 to 150°C, 290 to 300°F), where methanol, water, and mercaptans are removed.

3. Acid Processes

Treating petroleum products with acids is, like caustic treatment, a procedure that has been in use for a considerable time in the petroleum industry. Various acids, such as hydrofluoric acid, hydrochloric acid, nitric acid, and phosphoric acid, have been used in addition to the more commonly used sulfuric acid, but in most instances there is little advantage in using any acid other than sulfuric. The reactions of sulfuric acid with petroleum fractions are complex. The undesirable components to be removed are generally present in small amounts; large excesses of acid are required for efficient removal, which may cause marked changes in the remainder of the hydrocarbon mixture.

Paraffin and naphthene hydrocarbons in their pure forms are not attacked by concentrated sulfuric acid at low temperatures and during the short time of conventional refining treatment, but solution of light paraffins and naphthenes in the acid sludge can occur. Fuming sulfuric acid (*oleum*) absorbs small amounts of paraffins when contact is induced by long agitation; the amount of absorption increases with time, temperature, concentration of the acid, and complexity of structure of the hydrocarbons. With naphthenes fuming sulfuric acid causes sulfonation as well as rupture of the ring. Aromatics are not attacked by sulfuric acid to any great extent under ordinary refining conditions, unless they are present in high concentrations. However, if fuming acid is used or if the temperature is allowed to rise above normal, sulfonation may occur. When both aromatics and olefins are present, as in distillates from cracking units, alkylation can occur. Thus, as indicated, acid treatment of cracked gasoline distillate brings about losses due to chemical reaction and polymerization of some of the olefins to constituents boiling above the gasoline range. This makes redistillation necessary, and such losses may total several percent, even when refrigeration is employed to maintain a low temperature.

Acid treatment of high-boiling distillates and residua presents different problems. Most of these contain at least a small proportion of dissolved or suspended asphaltic substances, and almost all the acid comes out as sludge (*acid tar*); its separation is aided by the addition of a little water or alkali solution. However, there may be obvious chemical changes, such as sulfur dioxide evolution, and washed (acid-free) sludge from the treatment of practically sulfur-free oils may contain up to 10% combined sulfur derived from the treating acid. Although largely displaced for bulk production of both gasoline and lubricating oils, acid treatment still serves many special purposes. Paraffin distillates intended for dewaxing might receive light treatment to facilitate wax crystallization and refining, whereas insulating oils, refrigeration compressor oils, and white oils may be seated more severely. The sludge produced on acid treatment of petroleum distillates, even gasoline and kerosene, is complex in nature. Esters and alcohols are present from reactions with olefins; sulfonation products from reactions with aromatics, naphthenes, and phenols; and salts from reactions with nitrogen bases. In addition, such materials as naphthenic acids, sulfur compounds, and asphaltic material are all retained by direct solution. To these constituents must be added the various products of oxidation-reduction reactions: coagulated resins, soluble hydrocarbons, water, and free acid.

Disposal of the sludge is difficult, as it contains unused free acid that must be removed by dilution and settling. The disposal is a comparatively simple process for the sludge resulting from treating gasoline and kerosene, the so-called light oils. The insoluble oil phase separates out as a mobile tar-like material, which can be mixed and burned without too much difficulty. Sludge from heavy oil and bitumen; however, separates out as granular semisolids, which offers considerable difficulty in handling.

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Biographical Sketch

Dr. Speight has more than thirty years of experience in areas associated with the properties and processing of conventional and synthetic fuels. He has participated in, as well as led, significant research and development in refining heavy oil and coal, and related environmental issues. He has well over four hundred publications, reports, and presentations detailing these research activities and has taught more than forty related courses.

Dr. Speight is currently editor of the journal Petroleum Science and Technology (formerly Fuel Science and Technology International) and editor of the journal Energy Sources. He is recognized as a world leader in the areas of fuels characterization and development. Dr. Speight is also Adjunct Professor of Chemical and Fuels Engineering at the University of Utah.

Dr. Speight is the author/editor/compiler of more than twenty books and bibliographies related to fossil fuel processing and environmental issues. As a result of his work, Dr. Speight was awarded the Diploma of Honor, National Petroleum Engineering Society, for Outstanding Contributions to the Petroleum Industry in 1995 and the Gold Medal of Russian Academy of Sciences (Natural) for Outstanding Work in the Area of Petroleum Science in 1996. He has also received the Specialist Invitation Program Speakers Award from NEDO (New Energy Development Organization, Government of Japan) in 1987 and again in 1996 for his Contributions to Coal Research. Dr. Speight also received the degree of Doctor of Sciences from the Scientific Research Geological Exploration Institute (VNIGRI), St. Petersburg, Russia for Exceptional Work in Petroleum Science in 1997. In 2001, Dr. Speight was also awarded the Einstein Medal of the Russian Academy of Sciences (Natural) in recognition of Outstanding Contributions and Service in the field of Geologic Sciences.