

PETROCHEMISTRY AND OIL REFINING

Demercaptanization of Light Hydrocarbon Fractions with Strong Aqueous Ammonia without Producing Sulfur Caustic Wastewater

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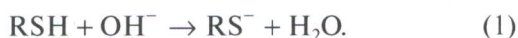
Abstract—A technology for the demercaptanization of light hydrocarbon fractions and liquefied petroleum gas with 25% aqueous ammonia is proposed. One advantage of this method for the demercaptanization of oil fractions over conventional processes such as Merox is the absence of a stage of oxidative catalytic recovery of spent caustic and highly toxic sulfur caustic wastewater. Spent (saturated with sulfur compounds) aqueous ammonia is recovered at the same plant for the distillation of sulfur ammonia wastewater in which aqueous ammonia is produced.

Keywords: liquified hydrocarbon gases, mercaptans, sweetening, strong aqueous ammonia, sulfur ammonia wastewater, sulfur caustic wastewater, wastewater treatment, hydrogen sulfide, ammonia

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INTRODUCTION

The most popular method for the demercaptanization of light hydrocarbon fractions and liquefied petroleum gas in oil refinery is currently the traditional caustic washing, which consists of the extraction of mercaptans¹ from the hydrocarbon phase into the aqueous phase by mixing petroleum products with a caustic solution. Being acidic compounds ($pK_a = 10–11$), mercaptans in the presence of hydroxide ions pass into the aqueous phase as salts—mercaptides:



Using a strong aqueous caustic (typically 15% NaOH) as an extractant in the industrial process requires a stage of catalytic recovery of the spent (saturated with sulfur compounds) caustic solution for its further use. The recovery uses atmospheric oxygen, by which the mercaptans passed into the aqueous phase are oxidized to disulfides, whereas the sulfides and hydrogen sulfide that are present are oxidized to thiosulfates, elemental sulfur, and sulfates. Disulfides are

then extracted from the spent aqueous caustic with an organic solvent (e.g., gasoline). Other water-soluble sulfur-containing compounds and carbonates that formed by the interaction of caustic with air containing carbon dioxide are accumulated in the circulating working caustic solution, reducing the free caustic concentration. Such spent caustic solutions cannot be efficiently sweetened, but are waste and should be disposed as highly toxic sulfur caustic wastewater (an alternative method for the demercaptanization of the working caustic solution to reduce the volume of sulfur caustic wastewater is distillation treatment [1]). Other disadvantages of the traditional technology, along with the formation of sulfur caustic wastewater, are the following:

(i) high irretrievable loss of caustic (with sulfur caustic wastewater) and catalyst (if a homogeneous catalyst introduced directly to the process was used),

(ii) the necessity of the qualified treatment of the air containing volatile sulfur compounds of various compositions,

(iii) the formation of corrosive elemental sulfur by the uncontrolled oxidation of the present sulfur compounds by atmospheric oxygen and the deposition of the sulfur on equipment components,

(iv) the necessity of a stage of extracting disulfides with the subsequent qualified treatment of the extract.

¹ Mercaptans are organic sulfur compounds with the overall formula RSH, where R is a hydrocarbon radical. In light hydrocarbon fractions and liquefied petroleum gas, which are considered in this work, R is typically CH₃ or C₂H₅. C₃H₇SH occurs rarely and in much smaller amounts. Heavier mercaptans are not encountered in these fractions.

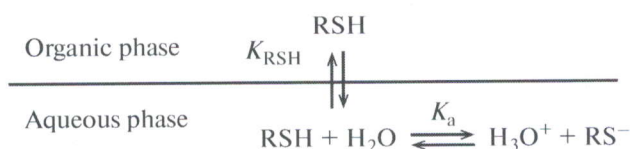
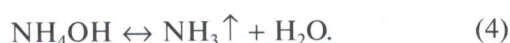


Fig. 1. Extraction system with weak acid RSH.

Thus, a stage of oxidative catalytic recovery of spent caustic is most problematic for each and every industrial process of caustic sweetening based on the extraction of sour sulfur from petroleum products with aqueous caustic, such as Merox, Mericat, and their various domestic analogs [2, 3]. Moreover, a system for caustic recovery and sulfur caustic wastewater disposal is most expensive to implement.

EXTRACTION OF MERCAPTANS WITH STRONG AQUEOUS AMMONIA

If caustic is replaced by 25% aqueous ammonia, then a stage of oxidative recovery of spent aqueous caustic is no longer necessary, because aqueous ammonia saturated with mercaptans and hydrogen sulfide can be completely recovered by heating to the boiling point. The mercaptans and hydrogen sulfide that have been extracted into the aqueous phase form ammonia salts (mercaptides $\text{RS}(\text{NH}_4)$, hydrosulfides NH_4HS , and sulfides $(\text{NH}_4)_2\text{S}$), which are readily decomposable (hydrolysable) while boiling. This enables one to recover the products of their hydrolytic decomposition as gases (ammonia, mercaptans, and hydrogen sulfide) and thereby completely recycle the aqueous ammonia by the reactions



Here, reactions (2) and (3) are written in short form without water.

Table 1. Material balance and key parameters of demercaptanization with aqueous ammonia by the example of treating BBFs

Parameter	Value
BBF flow rate, kg/h	34000
Aqueous ammonia (25 wt %) flow rate, kg/h	3500
Process temperature, °C	50
Pressure, MPa	1.4
Mercaptan sulfur content ($\text{CH}_3\text{SH} : \text{C}_2\text{H}_5\text{SH} = 4 : 1$) in BBFs:	
before treatment, ppm	300
after treatment, ppm	to 0

It is known that the extraction of weak acids, to which lower mercaptans belong, and, correspondingly, their distribution in the water-organic phase system depend on the pH of the aqueous phase (which underlies caustic sweetening). Mercaptan in this extraction system participates in two main equilibria (Fig. 1). On the one hand, 25% aqueous ammonia (pH 12.2) is a weaker base than 15% sodium hydroxide solution (pH 14); therefore, a priori, other conditions being equal, the degree of extraction of mercaptans with aqueous ammonia is lower than that with sodium hydroxide. However, the results of the extraction with aqueous ammonia after the optimization of the process conditions (the ratio, contact time, and dispersity of the interacting phases; the process temperature; etc.) can be no worse than those reached by the conventional caustic sweetening. Previously [4], a comparative study of the efficiency of the extraction of low-molecular-weight mercaptans (methyl, ethyl, and propyl mercaptans) with aqueous ammonia (25 wt % NH_4OH) and caustic (15 wt % NaOH) from model mixtures of light hydrocarbons and industrial samples of liquefied petroleum gas confirmed the possibility of using aqueous ammonia for the alkaline sweetening of light oil fractions and also determined the main features and parameters of extractive demercaptanization using aqueous ammonia instead of caustic by the example of the removal of light (C1-C3) mercaptans from the butane-butylene fraction in a standard process (Fig. 2).

Caustic sweetening in industry is typically carried out by continuous countercurrent extraction in a vertical column (extractor) equipped with internal contactors (trays, random or structured packing) to increase the efficiency of the interaction (maximize the contact area) of the mass-exchanging phases. The key parameters of the process are the process temperature, the extractant concentration, and the extractant-to-feed mass ratio. The extraction time (time of the interaction of the phases in the extractor) can be varied from 1 to 15 min, depending on the properties of hydrocarbon fraction and the extraction-process parameters.

As was determined [4], the high degree of removal of low-molecular-weight mercaptans (more than 99% of ethyl mercaptan and more than 80% of propyl mercaptan in continuous countercurrent extraction; methyl mercaptan is removed completely) is reached by preheating the extractant and hydrocarbon fraction to an optimal process temperature of 40–50°C and using aqueous ammonia with a concentration of no less than 25 wt % in the range of mass ratios of aqueous ammonia to hydrocarbon fraction from 1 : 10 to 10 : 1. The increase in the degree of extraction of low-molecular-weight mercaptans at temperatures above 20°C is caused by the intensification of the diffusion processes. A further increase in temperature (above 50°C) leads to a significant decrease in the degree of extraction of low-molecular-weight mercaptans. This

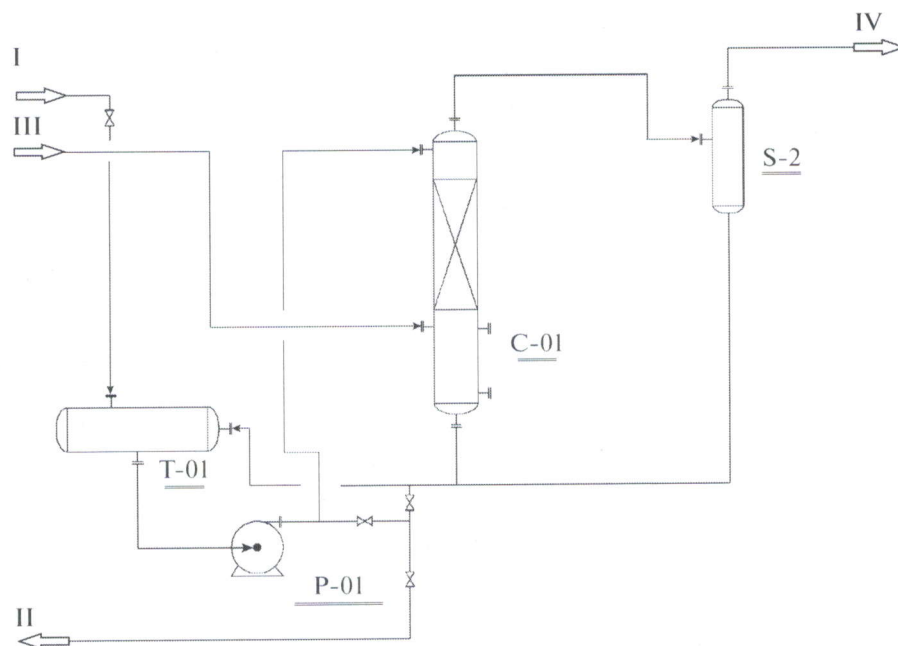


Fig. 2. Standard process of continuous countercurrent extraction of mercaptans from hydrocarbon fraction: (I) fresh aqueous ammonia (25 wt %), (II) spent (saturated with sulfur compounds) aqueous ammonia to recovery, (III) hydrocarbon fraction (light hydrocarbon fraction, liquefied petroleum gas, butane–butylene fraction, etc.) being treated, and (IV) treated (sweetened) hydrocarbon fraction. C-01, extraction column; T-01, surge tank; P-01, circulation pump; and S-2, water separator.

is related to an increase in the contributions of reactions of hydrolytic decomposition of the formed water-soluble salts (ammonium mercaptides) to form ammonia and the initial mercaptan, which is slightly soluble in the aqueous phase and very soluble in the hydrocarbon phase. The hydrolysis of ammonium mercaptides can be described by reaction (2), the equilibrium in which shifts to the right with increasing temperature.

Because aqueous ammonia is a weak base, using it at a concentration of less than 25 wt % significantly decreases the treatment efficiency. So does a decrease in the extractant-to-feed mass ratio below 1 : 10. Performing the process at extractant-to-feed mass ratios above 10 : 1 is impractical when there are large industrial amounts of hydrocarbon fractions to be treated.

The degree of extraction and, correspondingly, the residual content of sulfur-containing compounds can be controlled by varying the extraction temperature. Other process conditions being constant, by varying the extraction temperature within the range 30–60°C, one can achieve the incomplete removal of mercaptans. Because lower mercaptans are used as odorants—substances added to (naturally odorless) hydrocarbon gases to impart a characteristic smell to them, such a controlled demercaptanization process can simultaneously be a gas odorization process.

The proposed method efficiently uses aqueous ammonia to remove hydrogen sulfide and low-molecular-weight mercaptans from liquefied petroleum gas, propane–propylene and butane–butylene fractions,

natural gas liquids, straight-run gasolines, and catalytically cracked and other conversion gasolines.

Table 1 gives an example of the material balance and key parameters of demercaptanization of butane–butylene fractions (BBFs) with strong aqueous ammonia to reduce the concentration of light mercaptans from 0.03 wt % (240 ppm methyl mercaptan and 60 ppm ethyl mercaptan) to zero.

The experimentally determined extraction capacity of 25 wt % aqueous ammonia (extractant) at 50°C was 4.0 kg/t in extraction of ethyl mercaptan and 1.0 kg/t in the extraction of propyl mercaptan.

AQUEOUS AMMONIA RECOVERY

All the disadvantages of aqueous ammonia as an extractant in alkaline washing of hydrocarbon fractions due to its lower basicity (and, correspondingly, lower capacity to extract sulfur compounds) in comparison with sodium hydroxide can be readily compensated in most cases by the simplicity of its production and recovery in an oil refinery. Ammonia and aqueous ammonia can be obtained in a contemporary oil refinery in treatment of sulfur ammonia wastewater by the known distillation technology [5]. If an oil refinery has a facility such as a fresh aqueous ammonia source, this facility can also synthesize the recovery of spent (saturated with extracted sulfur compounds) aqueous ammonia by adding to the feed of the sulfur ammonia wastewater treatment plant (Fig. 3). The products of this plant are treated wastewater and gas-

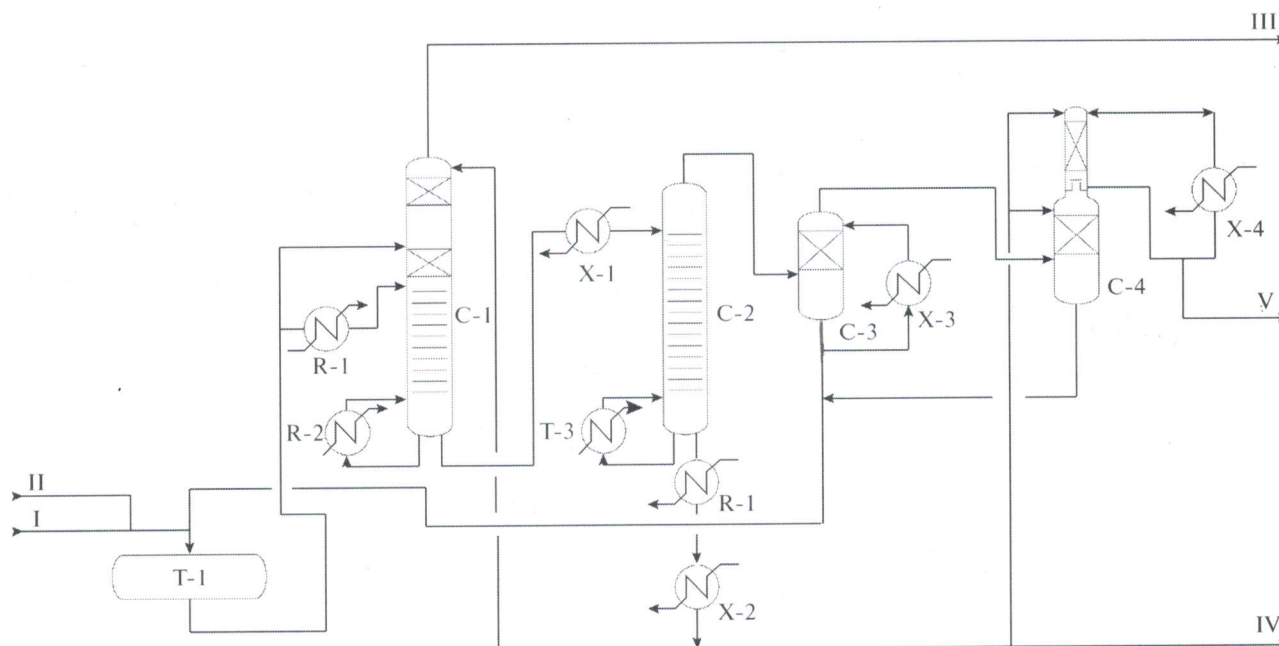


Fig. 3. Sulfur ammonia wastewater treatment plant producing aqueous ammonia: (I) sulfur ammonia wastewater, (II) spent aqueous ammonia from the demercaptanization plant, (III) hydrogen sulfide-containing gas, (IV) treated wastewater, and (V) aqueous ammonia (25 wt %). C-1, column of extraction of sulfur-containing compounds; C-2, wastewater treatment column; C-3, moisture content reduction column; C-4, aqueous ammonia production absorber; T-1, feed tank; X-1–X-4, coolers; and R-1–R-3, column reboilers.

eous hydrogen sulfide (feed for a sulfur and/or sulfuric acid production plant), ammonia, and/or aqueous ammonia. Depending on their amount and composition, mercaptans entering with spent aqueous ammonia either can be recovered with the gaseous hydrogen sulfide product flow (if their amount is relatively small and has no marked effect on either the Claus process or the sulfuric acid synthesis) or can be condensed and removed from the plant as an individual liquid phase (if their amount is sufficient). Fresh aqueous ammonia with a concentration of no less than 25 wt % is produced in and removed in a required amount from an absorber of a special design [6]. Along with being used for demercaptanization, aqueous ammonia can find a wide variety of applications for the needs of a contemporary oil refinery, e.g., for the selective noncatalytic reduction of nitrogen oxides (NO_x) in flue gases [7]. Excess gaseous ammonia (if any) can be disposed by qualified combustion using burners or incinerators of special design [8]. Such devices are typically combined with recovery boilers to produce steam for in-house needs, which strengthens the economic attractiveness of this method of integrated treatment of sulfur ammonia wastewater.

CONCLUSIONS

The presence of a plant of distillation treatment of sulfur ammonia wastewater to produce hydrogen sulfide and ammonia in an oil refinery [5] paves the way

for implementing the technology for sweetening (demercaptanization) light hydrocarbon fractions and liquefied petroleum gases with strong aqueous ammonia [9]. Spent (saturated with sulfur compounds) aqueous ammonia is recovered at the same sulfur ammonia wastewater treatment plant to obtain fresh aqueous ammonia, part of which is returned to the sweetening (demercaptanization) process, and to remove the extracted sulfur compounds (hydrogen sulfide and mercaptans) with the acid gas (hydrogen sulfide) product flow sent to disposal to a sulfur and/or sulfuric acid production plant.

If the amount of mercaptans entering with spent aqueous ammonia is sufficient, they can be removed from the plant as an individual product flow in the condensed state.

The main advantages of such a method of alkaline demercaptanization of liquefied petroleum gas and light hydrocarbon fractions are the elimination of the formation of difficult-to-dispose highly toxic sulfur caustic wastewater, the reduction of emissions to water and air, and more complete waste reuse owing to the creation of a zero-waste process.

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