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> PETROCHEMISTRY AND OIL PROCESSING

Treatment of Sulfide Alkali Waste Waters from Mercaptans Using Distillation

A. V. Anisimov^{*a*, *}, B. V. Andreev^{*b*}, E. A. Eseva^{*a*}, P. D. Polikarpova^{*a*}, A. V. Tarakanova^{*a*}, and A. S. Ustinov^{*b*}

> ^aMoscow State University, Moscow, 119991 Russia ^bIPOS Proekt LLC, Moscow, 117246 Russia *e-mail: sulfur45@mail.ru Received September 22, 2016

Abstract—Processes of methyl and ethyl mercaptan extraction from solutions simulating oil-refinery sulfide alkali waste waters have been studied by distilling argon in the air and atmosphere. In the latter case, the amount of ethyl mercaptan extracted from alkaline solution reaches 94%.

Keywords: sulfide alkali waste waters, mercaptans, treatment **DOI:** 10.1134/S0040579518040024

One of the main ecological problems for oil refinery and petrochemical enterprises is associated with the necessity of utilizing spent alkaline solutions and process steam condensates, which are contaminated with sulfides and collectively form so-called sulfide alkali waste waters (SAWWs). Large volumes of alkali solutions saturated with hydrogen sulfide and mercaptans are formed in the processes of alkali treatment (demercaptanization) of liquefied hydrogen gases and petroleum and kerosene fractions, as well as during the production of light olefins and pyrolysis gas treatment from hydrogen sulfide and carbon dioxide. In addition, secondary refining processes (catalytic cracking, hydrocracking, hydrotreatment, delayed cocking, etc.), where water vapor is used for process purposes, lead to the formation of hydrogen sulfide- and ammonia-contaminated water process condensates (sulfide-ammonium waste waters), which should also be locally treated (disinfected) before being discharged for the final all-factory biochemical treatment [1-3].

The presence of hydrogen sulfide and mercaptan in SAWWs makes these wastes highly toxic, which requires special measures to prevent the entry of these substances into the atmosphere and water bodies. The comprehensive solution to this problem is to maximally reduce the volume of SAWWS by introducing and improving regenerative processes, which will make it possible to sharply decrease the consumption of alkali for refining oil products based on its multiple use. In addition, the purpose of this method of SAWW regeneration is to remove as many absorbed sulfides (hydrogen sulfide and mercaptan) as possible from the flow so that the reduced alkali could be reused in the process of desulfurization, thereby decreasing operational costs and increasing the efficiency of technology. Processes of alkali demercaptanization are currently rather common and result in the formation of large volumes of highly toxic alkali waste waters, which should be utilized and detoxified; therefore, it is relevant to develop effective methods of SAWW regeneration [4-8]. The objective of this research was to study the applicability of the distillation method for regenerating sulfide alkali waste waters that are formed in industrial production during the alkali washing of liquefied hydrogen gases. For this purpose, model mixtures containing methyl and ethyl mercaptides of sodium were used. Regeneration was made using steam distillation and boiling methods in the presence and absence of inert gas.

EXPERIMENTAL PROCEDURE

The purity of the initial subjects was monitored and the composition of reaction products was analyzed by gas chromatography using a Kristall-2000M chromatographer equipped with a flame ionization detector (Zebron column L = 30 m, d = 0.32 mm, and ZB-1 liquid phase) at a temperature programmed from 50 to 150°C. The chromatograms were processed using Chromatec Analytic 1.5 software. The mercaptan concentration was determined by changes in the relative peak area of the substrate and products (in weight percentage).

Table 1. Results of experiments on the distillation of a model solution of sodium ethyl mercaptide with the absorption of mercaptan by dodecane and 10% solution of sodium hydroxide

Time, min	Share of ethyl mercaptan in absorbers, % of initial weight	Share of ethyl mercaptan in still, % of initial weight
60	63	30
120	69	15
240	75	6

Analysis conditions:

(1) nitrogen was used as a carrier gas (p = 200 kPa) and the volumetric flow rate was 30 mL/min;

- (2) the initial column temperature was 50° C;
- (3) the injector temperature was 150°C;
- (4) the detector temperature was 300° C;

(5) the surface heat rate was 10° C/min.

The study used distilled ethyl mercaptan (boiling temperature of 35°C), sodium methyl mercaptide (*Aldrich Chemical Company*), dodecane (chemically pure grade), sodium hydroxide (chemically pure grade), concentrated sulfuric acid, and concentrated orthophosphoric acid (chemically pure grade).

Preparing a Model Mixture of Sodium Ethyl Mercaptide

We prepared a solution with a weight fraction of sodium hydroxide of 20%, which corresponds to the alkaline solution used for extracting mercaptans at oil refineries. The stoichiometrically calculated amount of ethyl mercaptan was added drop by drop (1.55 g) to 5 g of a 20% water solution of sodium hydroxide until the alkali was completely neutralized. The flask was prepurged with argon to avoid the oxidation of the mercaptide solution by ambient oxygen to the respective disulfide. The weight fraction of the sodium ethyl mercaptide was 32% and the pH of the solution was 12.5.

Preparations of Model Mixture of Sodium Methyl Mercaptide

The sodium methyl mercaptide solution is prepared by dissolving sodium methyl mercaptide in water. To prepare 4 g of 28% sodium methyl mercaptide solution, it is necessary to use 1.12 g of pure sodium methyl mercaptide and dilute it with 2.88 mL of distilled water. The dilution is made in the inert argon atmosphere to avoid oxidation, a solution of sodium methyl mercaptide with a concentration of 28% is obtained, and the pH of the solution is 12.

Experiments on the treatment of model mixtures from mercaptans were carried out using standard laboratory equipment, which included a reflux condenser flask, a nozzle, and washers filled with absorption liquids (namely, dodecane and water solutions of sodium hydroxide). The choice of the absorber took into account its absorbing capacity and the ease of analysis (dodecane as an absorber makes it possible to analyze the content of mercaptan using gas-liquid chromatography without additional operations). The model solution was heated at reflux atmospheric pressure; the temperature of the plate was 200°C and the temperature in the flask was 100°C. The time at which the model mixture began intensively boiling was assumed to be the beginning of the experiment. Mercaptan is extracted by exposing the residue in the still to acid hydrolysis, followed by the successive addition of 2 g of dodecane and of the stoichiometrically calculated amount of 10% water solution of sulfuric acid.

RESULTS AND DISCUSSION

Oil-refinery sulfide alkali waste waters were simulated using water solutions of sodium methyl and ethyl mercaptides with a concentration of 32%, which corresponds to the maximum mercaptide concentration when mercaptan is completely absorbed by a 20% solution of sodium hydroxide in industries. As absorbers of mercaptans being extracted, we used dodecane, the retention time of which significantly differs from that for the mercaptans being analyzed under chromatographic conditions, as well as 10 and 20% water solutions of sodium hydroxide.

When the model alkaline solution of sodium ethyl mercaptide is boiled in air under reflux conditions for 3 h and for the period of capturing extracted ethyl mercaptan by dodecane, the residue in the still is 3.6% of the weight of the initial mercaptan in the solution and the amount of ethyl mercaptan absorbed by dodecane is 1.3% of the weight of the initial mercaptan. The bulk of ethyl mercaptan is entrained from the solution without being absorbed by dodecane and is partially oxidized to disulfide. The addition of another absorbernamely, a 10% solution of sodium hydroxide-to dodecane at the output in the process diagram (given the same boiling time, 3 h) makes it possible to increase the extraction of ethyl mercaptan to 75%, with the residue in the still being 6% of the weight of the initial ethyl mercaptan (Table 1).

The results show that the simple boiling of the model alkaline solution of mercaptan with the successive output capture of mercaptan by dodecane and a 10% solution of sodium hydroxide does not make it possible to capture more than 75% of ethyl mercaptan due to the insufficient absorbing capacity of dodecane.

Table 2. Results of experiments on the distillation of a model solution of sodium ethyl mercaptide in argon atmosphere with the absorption of mercaptan by 10 and 20% solutions of sodium hydroxide

Time, min	Share of ethyl	Share of ethyl	
	mercaptan in absorbers,	mercaptan in still,	
	% of initial weight	% of initial weight	
60	89	10	
120	92	6	
240	94	3	

Table 3. Results of experiments on the steam distillation

 of a model alkaline solution of sodium ethyl mercaptide

Time, min	Share of ethyl mercaptide in absorbers, % of initial weight	Share of ethyl mercaptan in still, % of initial weight
60	15	18
120	28	12
240	31	9

Table 4. Results of experiments on the influence of the duration of the boiling of an alkaline solution on the amount of mercaptan extracted from the solution

Time,	Conversion*	Conversion*
min	of methyl mercaptan, %	of ethyl mercaptan, %
20	69	58
60	91	89
120	94	92
240	95	94
360	95	96

* The conversion of mercaptan was calculated as the ratio of the weight of mercaptan extracted from absorbing solutions of mercaptan to the total weight of mercaptan in the initial alkaline solution.

The boiling of the model alkaline solution of sodium ethyl mercaptide in the argon atmosphere with the successive output capture of ethyl mercaptan by 10 and 20% solutions of sodium hydroxide makes it possible to reduce the amount of emitted ethyl mercaptan to 94% over the same time period (3 h) (Table 2).

The results of our research (see Table 2) indicate that the boiling of the model alkaline solution of sodium ethyl mercaptide in the argon atmosphere makes it possible to minimize the process of mercaptan oxidation and, therefore, significantly increase the amount of extracted ethyl mercaptan to 94%. When steam distillation in air was used, i.e., when a hot air flow was fed instead of argon, the results of ethyl mercaptan extraction do not reach even those values obtained during the simple boiling of the model alkaline solution in air (Table 3).

These results show that the basic losses of ethyl mercaptan during its extraction are due to its oxidation in the process of distillation in air. An increase in the duration of boiling of the model alkaline solution of mercaptan insignificantly influences the amount of mercaptan being extracted (Table 4).

The bulk of mercaptans is successfully removed from the alkaline solution during the first hour of regeneration. The further increase in the duration of the experiment does not lead to significant changes in the result. The concentration of the initial solutions of sodium methyl and ethyl mercaptides insignificantly influences the amount of extracted mercaptan. The results are given in Tables 5 and 6.

The content of free alkali is understood as a theoretical excess of alkali (given the excess of mercaptan) that exists in water solution and has not reacted with mercaptan according to diagrams (1) or (2):

$$NaOH + mCH_3SH \rightleftharpoons mCH_3SNa + (1 - m)NaOH + mH_2O,$$
(1)

Initial concentration of methyl mercaptide, %	Conversion of methyl mercaptide, %	Residual content of mercaptide, %	Content of free alkali in regenerated solution, % wt
8 (content of free alkali 13%)	79	1.7	15.8
16 (content of free alkali 8.6%)	85	2.4	17
28 (content of free alkali 0%)	91	2.5	18.2

Table 5. Dependence of conversion on the initial concentration of methyl mercaptide in the solution. Regeneration time of 1 h

Table 6. Dependence of conversion on initial concentration of ethyl mercaptide in the solution. Regener	eration time 1 h
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Initial concentration of ethyl mercaptide, % wt	Conversion of ethyl mercaptide, %	Residual content of mercaptide, %	Content of free alkali in regenerated solution, % wt
8 (content of free alkali 14%)	74	2.1	14.8
16 (content of free alkali 10%)	78	3.5	15.6
32 (content of free alkali 0%)	79	6.7	15.8

$$NaOH + mC_2H_5SH \rightleftharpoons mC_2H_5SNa$$

+
$$(1-m)$$
NaOH + m H₂O, (2)

$$0 \le m \le 1.$$

According to the data of this research, a decrease in the concentration of mercaptide in the initial source, other conditions being equal, leads to a decrease in the concentration of mercaptide, which is due to a shift in the equilibrium of hydrolysis reaction to the left due to a decrease in its concentration.

CONCLUSIONS

According to the data of our research, the optimal conditions for removing lower mercaptans from solutions simulating sulfide alkali waste waters are the distillation of the initial solution in the atmosphere of inert gas (argon) with the capture of extracted mercaptan by a water solution of sodium hydroxide.

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