

## Monitoring of condensate flows with a view to improving the quality of the odorant at U-30 of the OGPP

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### ABSTRACT

Currently, mercaptans are produced synthetically both in the domestic and foreign industry, which makes them cost high. The formation fluid of the Orenburg and Karachaganak fields processed at the Orenburg GPP is a rich raw material source of low-boiling natural mercaptans. Currently, the composition of the odorant is impermanent. It differs in the limits of boiling and the mixture ratios of natural mercaptans. The composition of the synthesized odorant includes a mixture of mercaptans from C1 to C4 and higher. The presence of methylmercaptan is undesirable as it reduces the intensity of the gas smell. In addition, the presence of heavy mercaptans from C4 and higher is also undesirable as they tend to hydrate formation. Since only C2-C3 mercaptans are to be present in the odorant, there arose a problem of removing or reducing the unwanted mercaptans. To solve this problem, an analysis of the flow of condensates entering the U-30 was carried out in order to obtain a quality odorant. The quality of the produced odorant was improved by the exception and selection of the optimal ratio of incoming condensate flows. The research is aimed at improving the quality of the odorant derived at the U-30 facility of the Orenburg GPP from light condensate fractions, where there is used a mixture of internal condensates from facilities U-741 (installation of condensate stabilization BX-04), U-374 (fractionation department of gas treatment plant E-18), U-40 (propane blocks, condensate of dehydration), U-11 (regeneration unit glagola, condensate of dehydration) after stabilizing at U-09 (hydrocarbon condensate processing plant), and also the absorbent from U-90 (plant for production of broad fraction of light hydrocarbons).

**Keywords:** *mercaptans, organosulfur, hydrolysis, sodium mercaptides.*

### 1. INTRODUCTION

In addition to the increase in gas and condensate production, there is a qualitative improvement in the utilized processing means, a comprehensive intensification of production, industrial development of new, progressive, economical technologies providing full and skilled use of all components that make up raw materials. These activities are aimed at the rational and integrated use of natural resources, in particular, organosulfur compounds – mercaptans [1-2]. The demand of the national economy for mercaptans is constantly growing. They are raw materials for the production of herbicides, defoliants, and feed proteins, they find their application in the petrochemical industry as inhibitors of coking and corrosion, and they are used in the gas and oil industry to odorize natural and associated gases in an individual form and in a mixture with sulfides and hydrocarbons [3-5].

Currently, mercaptans are produced synthetically both in the domestic and foreign industry, which makes them cost high. The formation fluid of the Orenburg and Karachaganak fields processed at the Orenburg GPP is a rich raw material source of low-boiling natural mercaptans.

Mercaptans account for the bulk of sulfurous compounds in light hydrocarbon fractions of the condensate of these deposits. For example, the light fractions of the stable condensate of the Orenburg field contain up to 2% mass. mercaptan sulfur [6-7].

The Orenburg GPP intensified internal processes that involved equipment; it led to a release of a part of the condensate stabilization facility U-30 (condensate stabilization unit). The facility helps extract a mixture of natural mercaptans from the stable condensate and its factions on an industrial scale. The extracted concentrate of the mercaptan mixture is used to odorize natural gas of household consumption.

Currently, the composition of the odorant is impermanent. It differs in the limits of boiling and the mixture ratios of natural mercaptans. The composition of the synthesized odorant includes a mixture of mercaptans from C1 to C4 and higher. The presence of methylmercaptan is undesirable as it reduces the intensity of the gas smell. In addition, the presence of heavy mercaptans from C4 and higher is also undesirable as they tend to hydrate formation. Since only C2-C3 mercaptans are to be present in the odorant, there arose a problem of removing or reducing the unwanted mercaptans [8-10].

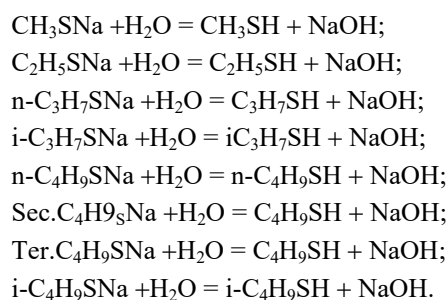
To solve this problem, an analysis of the flow of condensates entering the U-30 was carried out in order to obtain a quality odorant. The quality of the produced odorant was improved by the exception and selection of the optimal ratio of incoming condensate flows.

## 2. MATERIALS AND METHODS

The research is aimed at improving the quality of the odorant derived at the U-30 facility of the Orenburg GPP from light condensate fractions, where there is used a mixture of internal condensates from facilities U-741 (installation of condensate stabilization BX-04), U-374 (fractionation department of gas treatment plant E-18), U-40 (propane blocks, condensate of dehydration), U-11 (regeneration unit glagola, condensate of dehydration) after stabilizing at U-09 (hydrocarbon condensate processing plant), and also the absorbent from U-90 (plant for production of broad fraction of light hydrocarbons).

## 3. RESULTS

According to laboratory data, we determined the composition of sodium mercaptides, which is presented in Table 1.



In the hydrolysis of a mixture of mercaptans, the speed of the process is limited by the hydrolysis of sodium methylmercaptid. As a result of the regeneration process, C2-C4 mercaptans get regenerated completely and methylmercaptan does just by 80% [1].

The calculated number of mercaptans generated by the reaction is presented in Table 2.

This section may be divided by subheadings. It should provide a concise and precise description of the experimental results, their interpretation as well as the experimental conclusions that can be drawn.

The amount of generated caustic is 107.143 kg/h, and the amount of water that is consumed by reactions is 47.5841 kg/h. Based on the results, we drew a material balance of the regeneration stage taking into account the laboratory data. The balance is presented in Table 3.

In order to obtain the odorant, there is used a mixture of internal condensates from facilities U-741 (BX-04), U-374 (E-18), U-40 (condensate of dehydration), U-11 (condensate of

The U-30 regeneration column receives 26.47 m<sup>3</sup>/h of saturated caustic or 27 343.51 kg/h taking into account the density of the alkaline solution equal to 1033 kg/m<sup>3</sup>.

To increase the speed of hydrolysis, it is necessary to conduct the process at high temperatures and the lowest concentrations of sodium hydroxide in the solution. Pre-diluting sodium hydroxide solution with water by 15-50% of the volume before the heat exchanger (then the water circulates in the regenerator) allows increasing the degree of regeneration to 95%. At this facility, the amount of circulating water is 5.29 m<sup>3</sup>/h or 5290 kg/h [1].

dehydration) after stabilizing at U-09, and also the absorbent from U-90.

The obtained odorant contains mercaptans from C1 to C4 and higher. Its quality depends on the content of ethylmercaptan, i.e. the higher its content is, the better the quality is. To change the composition of the odorant, it is necessary to know the individual mercaptan content in each condensate entering the mixing.

To determine the individual components of RSH, we used a chromatograph "Varian Star 3400 CX", which is very sensitive to sulfurous compounds, so achieving even single peaks requires the selection of the desired ratio of sample and solvent (toluene), which was 1:5. As a result of the analysis, we get a chromatogram with different peaks that have a certain maintenance time and area.

To determine the conformity of each peak to a certain mercaptan, it is necessary to set the maintenance time of each individual mercaptan, so each individual standard mercaptan gets issued. The discovered maintenance times of individual mercaptans are presented in Table 4.

The maintenance time of isobutylmercaptan and n-butylmercaptan is determined relative to the maintenance time of secondary butylmercaptan.

Based on Table 4, we determined the quality composition of mercaptans in each condensate. To determine the quantitative composition, a standard mixture is prepared for the components that comprised the samples the most. In our case, the standard mixture was made from ethylmercaptan and isopropylmercaptan.

The standard mixture is presented on a chromatogram. The results of the condensate analysis on the content of individual mercaptans are presented in Table 5.

**Table 1.** The composition of sodium mercaptides

Sodium mercaptides	Mi	Gi	Ni=Gi/Mi	Gi'=Gi/ΣGi	Gi''=Ni/ΣNi	Mi*Gi''
		(kg/h)	kM/h	mass fraction	mole fraction	
CH <sub>3</sub> SNa	70	12.3	0.176	0.049	0.066	4.59
C <sub>2</sub> H <sub>5</sub> SNa	84	92.08	1.096	0.370	0.409	34.38
n-C <sub>3</sub> H <sub>7</sub> SNa	98	3.39	0.035	0.014	0.013	1.27
i-C <sub>3</sub> H <sub>7</sub> SNa	98	90.24	0.921	0.363	0.344	33.69
n-C <sub>4</sub> H <sub>9</sub> SNa	112	3.66	0.033	0.015	0.012	1.37
Sec.C <sub>4</sub> H <sub>9</sub> SNa	112	26.98	0.241	0.109	0.090	10.07
Ter.C <sub>4</sub> H <sub>9</sub> SNa	112	19.28	0.172	0.078	0.064	7.20
i-C <sub>4</sub> H <sub>9</sub> SNa	112	0.62	0.006	0.002	0.002	0.23
Sum		248.55	2.679	1.0	1.0	92.79

**Table 2.** The number of mercaptans generated by the reaction

Mercaptans	Mi	Gi, кг/т	Ni=Gi/Mi, км/ч	Gi'=Gi/ΣGi, mass fraction	Gi''=Ni/ΣNi, mole fraction	Mi*Gi''
CH <sub>3</sub> SH	48	6.7543	0.141	0.036	0.053	2.5551
C <sub>2</sub> H <sub>5</sub> SH	62	67.9639	1.096	0.362	0.415	25.71
n-C <sub>3</sub> H <sub>7</sub> SH	76	2.6202	0.034	0.014	0.013	0.9912
i-C <sub>3</sub> H <sub>7</sub> SH	76	69.979	0.921	0.372	0.348	26.472
n-C <sub>4</sub> H <sub>9</sub> SH	90	2.9446	0.033	0.016	0.012	1.1139
Sec.C <sub>4</sub> H <sub>9</sub> SH	90	21.6775	0.241	0.115	0.091	8.2004
Ter.C <sub>4</sub> H <sub>9</sub> SH	90	15.4959	0.172	0.082	0.065	5.8619
i-C <sub>4</sub> H <sub>9</sub> SH	90	0.5012	0.006	0.003	0.002	0.1896
Sum		187.9366	2.643	1.0	1.0	71.094

**Table 3.** The material balance of regeneration stage

Components	Income		Expenditure			
	Saturated caustic		Regenerated caustic		Odorant	
	kg/h	%mass	kg/h	%mass	kg/h	%mass
NaOH	437.5	1.600	543.24	2.000		
CH <sub>3</sub> SNa	12.3	0.045	2.45	0.009		
C <sub>2</sub> H <sub>5</sub> SNa	92.08	0.337				
n-C <sub>3</sub> H <sub>7</sub> SNa	3.39	0.012				
i-C <sub>3</sub> H <sub>7</sub> SNa	90.24	0.330				
n-C <sub>4</sub> H <sub>9</sub> SNa	3.66	0.013				
Sec.C <sub>4</sub> H <sub>9</sub> SNa	26.98	0.099				
Ter.C <sub>4</sub> H <sub>9</sub> SNa	19.28	0.071				
i-C <sub>4</sub> H <sub>9</sub> SNa	0.62	0.002				
Carbonate. caustic	109.37	0.400	109.37	0.403		
Na <sub>2</sub> S	33.75	0.123	33.75	0.124		
H <sub>2</sub> O	26514.34	96.968	26466.75	97.463		
CH <sub>3</sub> SH					6.754	3.5939
C <sub>2</sub> H <sub>5</sub> SH					67.963	36.163
n-C <sub>3</sub> H <sub>7</sub> SH					2.620	1.3942
i-C <sub>3</sub> H <sub>7</sub> SH					69.97	37.235
n-C <sub>4</sub> H <sub>9</sub> SH					2.944	1.5668
Sec.C <sub>4</sub> H <sub>9</sub> SH					21.677	11.534
Ter.C <sub>4</sub> H <sub>9</sub> SH					15.495	8.2453
i-C <sub>4</sub> H <sub>9</sub> SH					0.501	0.2667
Total:	27343.51	100.00	27155.57	100.00	187.94	100.00

**Table 4.** The discovered maintenance times of individual mercaptans

Components	Maintenance time, min.
Hydrogen sulfide	2.51 – 2.53
Methylmercaptan	2.67 – 2.71
Ethylmercaptan	2.89 – 2.93
Isopropylmercaptan	3.15 – 3.19
Tertiary butylmercaptan	3.54 – 3.58
N- propylmercaptan	3.61 – 3.64
Secondary butylmercaptan	4.25 – 4.31

**Table 5.** The condensate analysis on the content of individual mercaptans

Component	Component content, % mass					
	U-40 (condensate of dehydration)	U-741 (input capacity per unit-04)	U-11 (condensate of dehydration)	U-374 (E-18)	U-09 (condensate after stabilization)	U-90 (absorbent)
Methylmercaptan	4.81	10.50	6.58	7.00	n/a	6.08
Ethylmercaptan	23.77	20.23	28.5	26.62	22.71	26.16
Isopropylmercaptan	33.17	28.45	31.99	36.12	36.49	31.90
Tertiary butylmercaptan	8.32	11.68	7.92	8.63	10.62	8.04
N-propylmercaptan	7.02	4.79	6.92	8.87	11.13	7.85
Secondary butylmercaptan	18.67	20.35	14.98	10.13	15.02	16.61
Isobutylmercaptan	2.65	1.33	1.79	1.88	2.93	2.04
N-butylmercaptan	1.59	2.67	1.32	0.75	1.10	1.32
Sun	100	100	100	100	100	100

Component	Component content, % mass					
	U-40 (condensate of dehydration)	U-741 (input capacity per unit-04)	U-11 (condensate of dehydration)	U-374 (E-18)	U-09 (condensate after stabilization)	U-90 (absorbent)
Hydrogen sulfide	n/a	0.05	n/a	n/a	n/a	n/a
Content of ΣRSH in sample	1.64	0.91	1.67	3.60	2.33	2.01

**Table 6.** The composition of the odorant before and after the optimization of incoming condensate flows

Component	Component composition, % mass.	
	Before optimization	After optimization
methanethiol	3.21	N/a
ethanethiol	41.02	42.38
dimethyl sulfide	0.10	0.10
i-propanethiol	34.52	35.66
ter. butanethiol	1.28	1.32
n-propanethiol	7.46	7.71
sec. butanethiol	9.26	9.57
i-butanethiol	0.23	0.24
n-butanethiol	1.29	1.33
amount of hydrocarbons	0.27	0.28
Unidentified components	1.36	1.41
Total	100.00	100.00

#### 4. CONCLUSIONS

According to the results of studying the condensate flows intended to produce the odorant, the following conclusions can be drawn.

The presence of heavy mercaptans in the flows is a sum of C4-mercaptans of normal and isoform. The content of these mercaptans is approximately the same in all condensates as these condensates are from the light fraction of the stable condensate (t. C. C. - boiling point 180 C). Therefore, the removal or variation of condensate flows will not change the content of C4-mercaptans in the odorant. The composition of the odorant before and after the optimization of incoming condensate flows is presented in Table 6. All used condensates contain methylmercaptan, which is

undesirable in the odorant. But before entering the U-30 to receive the odorant, the flows from U-741 (BX-04), U-374 (E-18), U-40 (condensate of dehydration), U-11 (condensate of dehydration) are mixed and stabilized at U-09. As a result of the stabilization, one single flow gets released that does not contain methylmercaptan according to the results of the analysis. Therefore, there is only one flow from U-90 (absorbent) left that contains methylmercaptan and makes up a small part of the main flow.

Thus, in order to get rid of methylmercaptan in the odorant, it is necessary not to direct the absorbent from U-90 to U-30 to obtain an odorant, but to direct it to the commodity park for mixing with the stable condensate at U-110.

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