LOCAL CATALYTIC OXIDATIVE TREATMENT OF WASTEWATER

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Wastewater at the Moscow refinery undergoes biological treatment in general municipal treating facilities in the city of Lyublino. Therefore, particularly stringent requirements are imposed on the quality of the refinery wastewater in terms of contents of sulfides and phenols. Upon startup of the G-43-107 combination catalytic cracking unit, in which a process condensate (PC) is formed in amounts up to 12.5 m^3/h, with contents of sulfide sulfur up to 4000 mg/liter, the problem of wastewater treatment to remove sulfides has become particularly acute.

It was found that when the process condensate, preheated to 98°C, was purged with dry hydrocarbon gas (100 m^3 per m^3 of PC), the residual content of sulfide sulfur in the PC was reduced only to 500-1000 mg/liter. A section for treatment of the PC by purging was also incorporated into a KT-1 type unit for combined deep processing of crude oil at the Pavlodar refinery. In this unit, the content of sulfide sulfur in the PC before treatment averaged 5800 mg/liter, and after the treatment by purging 5300 mg/liter.

The unsatisfactory operation of this section for physical desorption of hydrogen sulfide by purging can apparently be attributed to the alkalinity of the PC, which had a pH of 8.3-8.9 before treatment and 8.7-9.8 after purging. According to data reported in [1, 2], sulfide sulfur at these levels of pH exists in the solution partly in the form of molecular dissolved hydrogen sulfide, which is readily purged, and partly in the form of nonvolatile hydrosulfide ions.

Another shortcoming of the purging process for PC treatment is that it consumes rather large amounts of energy, since a large amount of hydrocarbon gas and condensate must be heated to 95-98°C; also, the purge gas, which is contaminated with hydrogen sulfide and ammonia desorbed from the PC, must then be compressed and treated with monoethanolamine.

At the Moscow refinery, facilities have been installed for a process developed at VNIIUS [All-Union Scientific-Research Institute of Hydrocarbon Feedstocks] for local catalytic oxidative treatment of wastewater (LCOTW) consisting essentially of liquid-phase oxidation of toxic sulfides to less harmful thiosulfates, using atmospheric oxygen in the presence of a phthalocyanine catalyst KS-1 on a polyethylene base [3]. This process was introduced by reconstructing a unit for the treatment of sour caustic waste, where these waters had been treated (0.5 m^3/h) successively in three towers by noncatalytic oxidation with air at 95-100°C, with an air input of 500 m^3/h.

Use of the KS-1 catalyst made it possible to treat the same volume of SCW and also the entire volume of PC from the G-43-107 unit in a single tower with a diameter of 1.8 m and a height of 19.98 m, charged with KS-1 catalyst prepared in the form of 50-mm diameter Pall

TABLE 1

Tower temperature, °C	Flow rates			H_2S content, g/liter		Content of phenols, mg/liter	
	condensate, m^3/h	SCW, m^3/10 days	air, tonnes per h	at inlet	at outlet	at inlet	at outlet
79,7	9,49	12,8	375	2,08	0,02	135,0	124,6
76,5	10,50	60,8	341	2,05	0,05	195,7	158,3
77,6	10,19	19,2	400	1,39	0,013	182,0	153,2
77,9	10,30	94,4	400	1,93	Отс.	241,4	142,7
79,2	12,10	67,2	373,7	2,14	0,026	192,2	138,2
63,3	6,82	41,6	332	2,42	0,09	98,8	75,7

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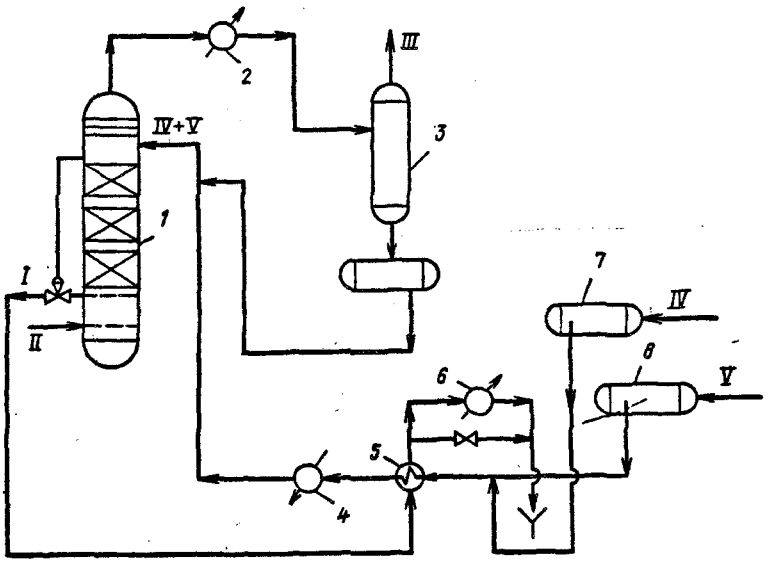

Fig. 1. Process flow plan of unit for combined treatment of process condensate from G-43-107 unit and sour caustic waste: 1) oxidation tower; 2, 6) coolers; 3) separator; 4) steam-heated exchanger; 5) heat exchanger; 7, 8) tanks; I) oxidized PC; II) air; III) spent air; IV) SCW; V) PC from G-43-107 unit.

rings charged to the tower in three beds with a height of 2.5 m each. The catalyst operates in the bubbling regime and also plays the role of effective packing in the reactor, facilitating dispersion of the air and improving the mass transfer between the streams being treated, the atmospheric oxygen, and the catalyst surface.

As shown in Fig. 1, the process condensate V from the G-43-107 unit is pumped from a surg tank through a pipeline to the SCW treating unit, entering the tank 8, and thence through the heat exchanger 5 and steam-heated exchanger 4, where it is heated to 75-80°C and then enters the top of the oxidation tower 1. The bottom of the tower is fed with untreated air II (30-40 m^3 per m^3 of wastewater). The spent air III, containing up to 0.7 g/m^3 of hydrogen sulfide and ammonia, passes through the water cooler 2 and separator 3 to the calcination furnace of a sulfur production unit.

The oxidized PC I is withdrawn from the bottom of tower 1 through a flow controller into the heat exchanger 5, where it gives up heat to the untreated condensate, then passing through the cooler 6 or bypassing the cooler and proceeding directly to the sewer line. The sour caustic waste IV, as it accumulates in the receiving tank 7, is pumped into the line and blended with the PC (no more than 1 m^3/h).

Commercial operation of the LCOTW unit at the Moscow refinery for a period of more than 1.5 years has demonstrated the operating capabilities of this unit. During this time, the activity of the SK-1 catalyst has remained essentially unchanged. The degree of removal of sulfides from the PC has been greater than 90% during the entire period of operation (see Table 1); the average content of phenols in the wastewater has been lowered 30% relative to the original level.

The expected saving due to the introduction of the LCOTW process is about 100,000 rubles per year as a result of saving of energy resources in treatment, in comparison with the previously used process. On the basis of the results that have been obtained, the LCOTW process can be recommended for treatment of process condensate in all catalytic cracking units.

LITERATURE CITED

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