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Optimizing the use of oil gases released during processing

Optymalizacja wykorzystania gazów ropopochodnych uwalnianych podczas rafinacji

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ABSTRACT: The issue of using oil gases is considered because the removal of harmful substances from gases produced during oil refining, and thus and purification of these gases, are critical issues. In the catalytic cracking purification system, where hydrogen-containing gas circulates, the presence of hydrogen sulfide in the gas fractionation unit poses a challenge. Additionally, corrosion of equipment and pipelines during transportation causes environmental pollution. The presence of hydrogen sulfide and carbon dioxide in the gas complicates processing process, making their removal from the gas composition essential. To achieve this, methods such as chemical absorption, physical absorption, combined absorption, oxidation, and absorption by solid absorbents are employed. The use of amines is one of the important indicators of wastewater treatment plants. The presence of a certain amount of H_2S in the hydrogen-containing gas circulating in the hydrotreating unit reduces catalyst activity in reactors and leads to equipment failure. In a catalytic cracking unit, harmful components are absorbed by absorbents. Technological calculations of the indicators and modes of the main apparatuses of the absorption and desorption processes were carried out, with the results presented in tables. These calculations focus on column-type devices, separators, heat exchangers, and coolers, enabling the purification of gas contents using cold absorption and desorption processes. The use of a 15% aqueous solution of monoethanolamine proved most effective for hydrogen sulfide separation. The operating modes of the blocks in which these processes are carried out have been studied. The study also examines the transformation of sulfur compounds into paraffin, naphthenic and aromatic hydrocarbons, depending on the structure of the hydrocarbon chain, with hydrogen sulfide being released during hydrogenation under pressure. Improvements in the quality of dry gas transportation have significantly enhanced the efficiency of both transportation and processing.

Key words: catalytic reforming, catalytic cracking, hydrotreating, desorption, absorbent, monoethanolamine, dry gas, absorption.

STRESZCZENIE: Zagadnienie wykorzystania gazów ropopochodnych jest rozpatrywane z uwagi na fakt, że usuwanie szkodliwych substancji z gazów powstających podczas rafinacji ropy naftowej, a tym samym oczyszczanie tych gazów, ma niezwykle ważne znaczenie. W instalacji oczyszczania krakingu katalitycznego, gdzie krąży gaz zawierający wodór, obecność siarkowodoru w jednostce frakcjonowania gazu stwarza istotne problemy. Ponadto korozja urządzeń i rurociągów podczas transportu powoduje zanieczyszczenie środowiska. Obecność siarkowodoru i dwutlenku węgla w gazie komplikuje proces przetwarzania, a tym samym niezbędne jest ich usunięcie z gazu. W tym celu stosuje się metody takie jak absorpcja chemiczna, absorpcja fizyczna, absorpcja kombinowana, utlenianie oraz absorpcja przez absorbenty stałe. Zastosowanie amin jest jednym z istotnych wskaźników oczyszczania ścieków. Obecność pewnej ilości H_2S w gazie zawierającym wodór, krążącym w jednostce hydrorafinacji, obniża aktywność katalizatora w reaktorach i prowadzi do awarii urządzeń. W systemie katalitycznego krakingu szkodliwe składniki są wchłaniane przez absorbenty. Przeprowadzono obliczenia technologiczne wskaźników i trybów pracy głównych aparatów procesów absorpcji i desorpcji, a wyniki przedstawiono w tabelach. Obliczenia te dotyczą urządzeń kolumnowych, separatorów, wymienników ciepła i chłodnic, umożliwiając oczyszczanie gazu przy użyciu procesów absorpcji i desorpcji w niskiej temperaturze. Najskuteczniejsze w separacji siarkowodoru okazało się użycie 15% wodnego roztworu monoetanoloaminy. Zbadano tryby pracy bloków, w których realizowane są te procesy. Analiza obejmuje również przekształcanie związków siarki w węglowodory parafinowe, naftenowe i aromatyczne, w zależności od struktury łańcucha węglowodorowego, z uwalnianiem siarkowodoru podczas uwodornienia pod ciśnieniem. Poprawa jakości transportu gazu suchego znacząco zwiększa efektywność zarówno transportu, jak i przetwarzania.

Słowa kluczowe: reforming katalityczny, kraking katalityczny, hydrorafinacja, desorpcja, absorbent, monoetanoloamina, gaz suchy, absorpcja.

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Introduction

The natural and associated gases, and gases produced during oil refining processes contain a wide range concentration (from a few ppm to several tens of ppm) of aggressive components such as hydrogen sulfide (H_2S) and carbon dioxide (CO_2). These impurities can lead to equipment and pipeline corrosion, as well as environment and catalysator pollution during refining (Abbasov et al., 2013, 2015). The presence of sulfurdioxide formed from these gases poses a significant hazard to the environment. At the same time, hydrogen sulfide, used on a large scale in industry, serves as a valuable raw material sulfur production.

CO_2, often considered a ballast in gas streams, increases transportation costs and complicates gas treatment. In some cases, the presence of CO_2 leads to the formation of hydrate compounds, causing operational challenges. Therefore, the removal aggressive components from both economic and environmental gases is of great importance (Kuznetsov, 2002; Kuznetsov et al., 2012; Skoblo et al., 2013).

The selection of gas scrubbing method for aggressive components depends on the composition and parameters of the raw material, the required treatment level, the production field, energy resources, etc.

Globally, large-scale gas processing methods are commonly used. From smaller gas flows, oxidation and adsorption processes are typically employed.

Research methodology

Currently, the following methods are employed to remove aggressive components from gases:

- H_2S and CO_2 react with the active part of the absorbent;
- Physical absorption – acid components dissolve in organic absorbents;
- Combined – chemical and physical absorbents are used together;
- Oxidation – based on sulfur or H_2SO_4 in absorbed H_2S;
- Adsorption – absorption of components by solid absorbents.

Industrial requirements for absorbents include high absorption capacity, low vapor pressure, chemical and thermal stability, low-setting and heating capacity, minimal corrosivity, selectivity, and non-toxicity (Khloptsev, 2012). Absorbent properties such as absorption capacity and viscosity affect the energy consumption for circulation.

Absorbents with lower vapor pressure and greater stability minimize losses. Corrosion properties influence the choice of materials for equipment in gas removal units. In physical absorption, the required absorbent amount is nearly independent of impurity levels in the initial gas (according to Henry's law).

In the process of chemisorption, the amount of absorbent is proportional to the amount of mixture. This pattern defines the difference between chemical absorption and physical absorption.

Globally, amine-based processes are widely used to purify gases from aggressive components. Ethanolamines-monoeranolamine (MEA), diethanolamine (DEA), triethanolamine (TEA), diglycolamine (DQA), etc., are used as absorbents for gas purification from H_2S and CO_2. Of these, mono- and diethanolamines are the most commonly used.

TEA is less frequently used because of its low absorption properties. Other amines are used for selective removal of aggressive components (Bondarenko, 2003; Aliyeva et al., 2015) The mechanism of H_2S and CO_2 absorption by amines aqueous solutions follows below reactions:

H_2S + [amine] = [amine H]$^+$ + HS

CO_2 + 2[amine] = [amine H] + [amine COO]

$CO_2 + H_2O = H_2CO_3$

$H_2CO_3 = H^+ + HCO_3$

$HCO_3 = H^+ + CO^3$

[amine] + H^+ = [amine H]

As a result of the combining amines with H_2S, amine sulfide or hydrogen sulfide is formed, the reaction is instantaneous.

Mono- and diethanolamines react with CO_2 to form carbonates (amine COO – H^+). Carbonates and bicarbonates of amines are also obtained with CO_2. The dissolution of CO_2 in water also generates carbonic acid (Yuriev, 2009; Gartman, 2017).

Amine carbonates are unstable and slowly decompose in weak alkaline environments to form bicarbonates:

$R_2NCOOR_2NH_2 + H_2O = R_2NH + R_2NH_2HCO_3$

Pure amines are highly viscous liquids and have high freezing points. However, their aqueous solutions exhibit low viscosity and low freezing point (below –10°C). Therefore, aqueous solutions of ethanolamines are used as absorbents for purification of gases from aggressive components through the absorption method (Agilent Texnologies, 2006–2007; Afanasyev et al., 2018).

The concentration of amines in the solution can vary widely and is selected based on research results and corrosion control.

One of the key indicators of gas treatment plants is the consumption of amines. Therefore, the price of absorbents is very expensive and accounts for most of the operating costs.

Results and their discussion

Gases produced in certain oil and gas fields of our republic sometimes contain small amounts of hydrogen sulfide and other

Table 1. Compilation of information on the kalon type device
Tabela 1. Zestawienie informacji o urządzeniu typu kalon

Unit	Working conditions				Casing height [m]	Casing diameter [m]
	T [°C]	P [MPa]	Flow rate [t/hour]			
			fluid	vapor		
For hydrogen-containing gas:						
upper part	38	3.2	–	28.7	18.40	1.9
lower part	42	3.2	31.7	–	–	–
For dry gas:						
upper part	38	1.1	–	10.3	19.60	1.1
lower part	43	1.1	16.1	–	–	–
Regeneration of MEA solution:						
upper part	115	0.3	–	1.8	26.17	2.1
lower part	125	0.3	65.0	–	–	–

Table 2. Information on separators
Tabela 2. Dane dotyczące separatorów

Unit	Environment	Flow [t/hour]	Working conditions		Basic dimensions			Gas storage time separator [min]
			T [°C]	P [MPa]	volume [m^3]	diameter [M]	height [M]	
For hydrogen-containing gas	Purified hydrogen gas	30.00	42	3.1	16.5	2.0	5.2	0.25
For dry gas	Refined dry gas	11.50	42	1.5	4.5	1.2	4.5	0.23
For acid gas	Acid gas	0.98	42	0.2	6.5	1.2	5.5	0.23

sulfur compounds. However, significant levels of hydrogen sulfide are present in gases obtained during the processing of low-sulfur oils in oil refineries. Thus, the hydrogen-containing gas produced in the catalytic reforming unit and circulated in the diesel fuel hydrotreatment process, as well as the dry gas generated in the catalytic cracking unit, can contain up to 2% hydrogen sulfide.

The component composition of hydrogen-containing gas is given below:

Components	[% mass]
Hydrogen	83.50
Methane	5.90
Ethane + ethylene	5.41
Propane + butylene	0.23
Butane + butylene	0.68
Pentane	0.10
CO_2	1.10
H_2S	1.76
Total	100.00
Density, kg/m^3 at 20°C	0.291

The component composition of the dry gas from the catalytic cracking unit is shown below.

Components	[% mass]
Methane	43.56
Ethylene	16.90
Ethane	1.78
Propylene	7.02
Propane	1.65
i-Butane	2.12
i-Butylene + butylene-1	0.93
n-Butane	0.81
trans-Butylene	0.43
tank-Butylene	0.35
3-Methylbutene-1	0.02
i-Pentane	1.51
pentane-1	0.02
3-Methylbutene-1	0.07
n-Pentane	0.99
trans-Pentane-2	0.06
tank-Pentane-2	0.03
2-Methylbutene-2	0.11
hexane (C_2)	0.02
O_2	0.0006
N_2	0.0029
CO_2	0.0200
H_2S	1.50
Density, at 20°C [kg/m^3]	0.956

The presence of a significant amount (2%) of H_2S in the hydrogen-containing gas circulated in the hydrogen purification unit causes a decrease in the activity of the catalysts in the reactors, a decrease in the efficiency of the process, and corrosion of the equipment. The dry gas received in the absorption and gas fractionation units of the catalytic cracking unit is currently being transported to "Ethylene-Polyethylene" plant of SOCAR for processing. The presence of up to 1.6% H_2S in the content of this gas results in the corrosion of the equipment of the transportation system and technological facilities, the reduction of the efficiency of the processing processes, and the reduction of the quality of the received products. Therefore, the elimination of H_2S from these gases is of special importance. For this purpose, it is proposed to use the absorption process.

The process of gas purification from hydrogen sulfide by the absorption method consists of two blocks – absorption and regeneration of the saturated MEA solution.

15% aqueous solution of MEA is intended to be used as an absorbent. Some of the properties of this solution are given below.

Density [kmol/m^3]	2.4
Boiling temperature [°C]	112
Freezing temperature [°C]	–5
Viscosity, at 40°C, 103 Pascals	1.0
Vapor pressure at 40°C [kPa]	6.7

The main technological scheme of the proposed unit for the purification of gases by the absorption method is shown in Figure 1.

Hydrogen containing up to 2.05 H_2S is transferred to absorber 2 in line I at a pressure of p = 3.2–3.5 MPa and a temperature of t = 40°C. To remove sulfur compounds from the gas, a 15% aqueous solution of MEA is supplied to the upper part of the absorbent through the V-line using the N-1/1.2 pump.

The purified gas is freed from MEA particles after passing through the separator 1 and is transferred to the hydrocleaning unit of the catalytic cracking unit through line III.

The dry gas, containing 1.6% H_2S, received from the absorption and gas fractionation section of the catalytic cracking unit, enters the absorber 3 at a pressure of p = 1.1–1.4 MPa and a temperature of t = 40°C through line II to be purified from hydrogen sulfide. A 15% aqueous solution of MEA is supplied to the upper part of the absorber from tank 5 through line VI and pump N-2/1.2 for the removal of H_2S from the gas content.

The gas purified in the absorber from MEA particles after passing through separator 4 and transported to SOCAR's Ethylene-Polyethylene plant for further processing through line IV.

The MEA solution saturated with hydrogen sulfide from absorbers 2 and 3 is supplied to tank 6 through line VIII. After

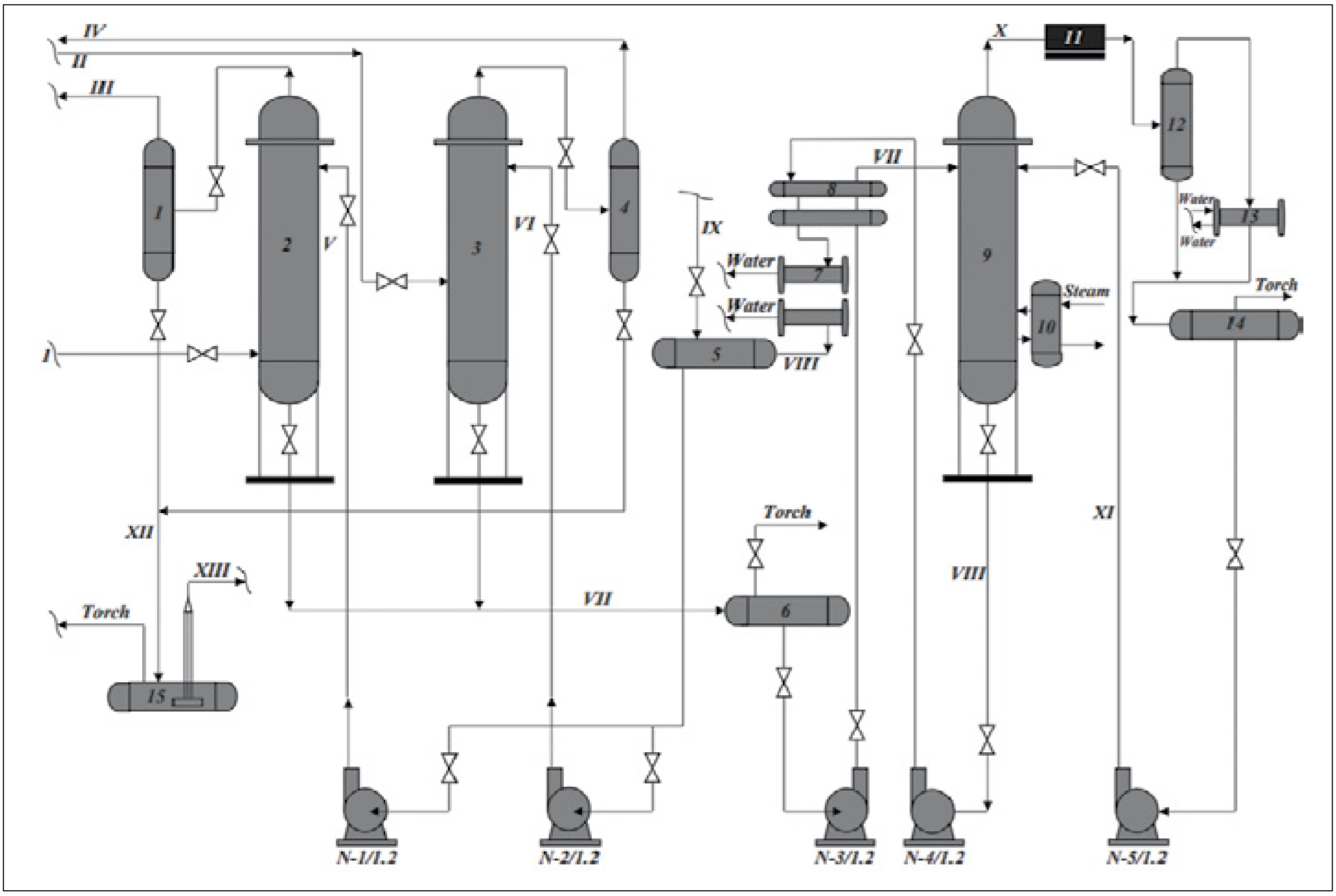

Figure 1. The principle technological scheme of the hydrogen-containing gas purification unit

Rysunek 1. Podstawowy schemat technologiczny urządzenia do oczyszczania gazów zawierających wodór

Table 3. Report data on heat exchangers and chillers
Tabela 3. Dane raportowe dotyczące wymienników ciepła i agregatów chłodniczych

Unit	Direction of flows	Environment	Flow [kg/hour]	Temperature [°C]		Heat load [10^3c/hour]	Heat transfer coefficient, *C* [m^3hour°C]	Surface area [m^2]
				access	exit			
Saturated MEA solution heat exchanger	Pipe area	Regenerated MEA solution	55 000	122	62	9506521	842.00	420
	Annular area	Saturated MEA solution	54 856	42	90			
Water cooler of regenerated MEA solution	Pipe area	Water	42 000	30	45	5090630	606.50	691
	Annular area	Regenerated MEA solution	55 000	65	35			
Water cooler of a mixture of water vapor condensate and H_2S	Pipe area	Water	1 000	30	35	39431.103	205.50	36
	Annular area	Hydrogen sulfide	856	42	35			
Air condenser-cooler	Pipe area	Water vapor	1 108	110	45	2602031	101.25	826
	Annular area	Hydrogen sulfide	856					

being heated to 90°C, it is transferred to the desorbent 9 through line VII. The temperature below the desorber is 120°C, while above it – 110°C.

The heat for the bottom part of the desorber is supplied by 10 evaporators using water vapor at a pressure of 1.0 MPa. Hydrogen sulfide and water vapor exiting the top of the boiler are cooled in air condenser-cooler II through line X and collected in tank 14. The separated gas (H_2S) is transferred to the flare system, while the liquid is supplied to the top of the desorber through line XI by pump N-5/1.2.

The regenerated MEA solution is transferred from the desorber to the pipe area of the heat exchanger through line VIII using pump N-4/1.2. It is cooled to 62°C and then further cooled to 40°C in water cooler before being returned to tank 5.

In the case of repairs or accidents, the liquid phase in separators 1 and 4 is transferred to drain tank 15 through line XII, and then to tank 6 through line XIII.

To maintain the required concentration of circulating MEA solution during gas purification from hydrogen sulfide, additional MEA solution is periodically injected into the system through line IX.

Technological calculations were conducted to determine the indicators and operating modes of the main apparatus involved in the absorption and desorption processes. The flow rates were 100 000 nm^3/hour for hydrogen-containing gas and 110 000 nm^3/hour for dry gas was.

Generalized data from these calculations are presented in Table 1 for casing-type devices, Table 2 for the separator, and Table 3 for the heat exchanger and coolers.

It should be noted that the distance between the 24 valved, single-flow, disk-shaped plates in the casing-type devices was 0.6 m.

Conclusions

It is proposed to use absorption and desorption processes to remove hydrogen sulfide from hydrogen-containing and dry gases.

On the basis of the developed new technology, the design documents of the device for hydrogen sulfide removal from hydrogen-containing and dry gases in the catalytic reforming and catalytic cracking units have been developed and approved for application.

The application of this device will allow to reduce the amount of H_2S in the content of hydrogen-containing gas to 500 ppm, and in the content of dry gas to 100 ppm.

In case of dry gas transportation, the quality of transportation increases, the pipe is not blocked by plugs, gas losses are reduced, and the efficiency of transportation and processing increases.

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