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UTILIZATION OF HYDROGEN SULFIDE-CONTAINING REFINERY FLARE GASES

Abstract. Modern oil refinery flare does not provide the beneficial use of discharged hydrocarbon gases and vapors, which does not allow to reduce the volume of hydrocarbon gas burned in flare candles and reduce atmospheric pollution. To ensure a stable and trouble-free operation of the flare plant and to increase the efficiency of waste gas utilization, their preliminary compression using mechanical or jet compressors and the construction of gas treatment plants are required. A low-cost method of utilizing hydrogen sulfide-containing refinery gas is proposed, including two-stage gas compression by a liquid-ring compressor using an alkanolamine aqueous solution as a working fluid in the first stage of compression, separation of the compressor of first stage compression to produce desulfurized gas, hydrocarbon condensate and an alkanolamine saturated hydrogen sulfide. In the second stage, the compression of the desulfurized gas is carried out by a liquid-ring compressor using a hydrocarbon absorbent as the working fluid, cooling and separation of the compress of the second stage of compression produce lean gas, water condensate and absorbate. The aqueous condensate is mixed with saturated hydrogen sulfide alkanolamine absorbent and taken out for regeneration, the hydrocarbon condensate is mixed with the absorbate to produce BFLH, and the lean gas is subjected to membrane separation to produce hydrogen and fuel gas. Application of the method can partially cover the needs of refineries in hydrogen by reducing its losses, as well as return gas and hydrocarbon fractions for processing or to the fuel network of the plant.

Key words: flare plant, oil refining, waste gases, hydrogen sulfide, gas purification, gas compression, liquid-ring compressor, hydrogen utilization, fuel gas.

The relevance of the topic. Flare systems are designed to ensure the safety of permanent, periodic, and emergency discharges of flammable gases and vapors with their subsequent combustion. The most widely used method for gas utilization in flare plants is gas separation, which involves the separation of flare gases to produce hydrocarbon gas, which is utilized for combustion, and condensate that is pumped out of the plant. The modern flare facility of the oil refinery includes special installations for collection, short-term storage, and return of released hydrocarbon gases and vapors for further use. This method reduces the volume of irreversible losses of hydrocarbon gas (burned in flare candles), thereby reducing atmospheric pollution, and ensures stable and trouble-free operation of the flare plant [1-4]. Given that the emission of flare gas is one of the main sources of environmental pollution and global warming, it is of great importance to develop the methods for utilization of flare gases in the oil and gas industry, in particular in oil refineries of many countries [5-8]. One of the problems related to the utilization of low-pressure flare gases is the need to compress them to the pressure necessary for processing or transportation to external consumers [9-11].

Discussion of problems. For compression of hydrocarbon gas in flare plants, piston and screw compressors are usually used. To drive them, a large amount of energy resources (electricity or water vapor) is consumed, moreover, one could observe hydrogen sulfide corrosion of internal components, parts of the compressor, and other installation, pollution of the production environment due to leakage of the compressed medium [12-13]. As an alternative to a mechanical system for compressing flare gas, liquid-jet compressors are proposed. Water, petroleum products, and crude oil are used as the working fluid of a jet compressor (JC), and in the case of compression of aggressive gases, neutralizing liquids are used. For example, it is reported that light coking gasoil is used as a working fluid to compress the flare gas to a pressure of 0.5-0.6 MPa, which allows to send it to the fuel network of the plant. C3+ hydrocarbon fractions are released from the flare gas during compression due to their dissolution in gasoil and diverted to the catalytic cracking unit for utilization along with the balance excess [14].

The disadvantage of using gasoil or other petroleum products as a working fluid is that they practically do not absorb hydrogen sulfide during the gas compression process. The presence of its residual amounts in the compressor, which is used as fuel in process furnaces, leads to contamination of the production environment with toxic sulfur dioxide. To combine the processes of compression and purification of gas from hydrogen sulfide in a jet compressor, it is proposed to use an aqueous solution of amine as the working fluid [13]. However, as the practice has shown, the amine solution is contaminated with heavy hydrocarbon fractions contained in the compressed gas, which complicates the process of regeneration of the solution due to the foaming in the desorption column.

From both economic and operational points of view according to foreign companies, it is more appropriate to use low-pressure refinery gases for compression, including flare gases, and liquid-ring compressors (LRC). They successfully solve the problem of compressing explosive gases, as well as gases with a high content of hydrogen sulfide, hydrocarbon condensate, water, and gases containing mechanical impurities [15-17].

This type of compressor (LRC) supplied mainly by foreign manufacturers finds its application in the Russian oil and gas production and refinery [18-19]. For example, Garo and several other foreign companies supply compressors and installation based on them for the utilization of hydrogen sulfide-containing flare gases that use alkanolamine solutions as the working fluid. Due to the absorption properties of the working fluid in relation to hydrogen sulfide, these installations (see figure 1) reduce its content in the compressed fuel gas, which helps to solve the problem of environmental protection. When compressing the flare gas, heavy hydrocarbons of gasoline fractions are partially released from it because of condensation, which is usually carried with the gas to the flare. However, the use of an amine solution as a working fluid does not limit the loss of hydrogen contained in refinery flare gases in an amount of up to 60% vol., the loss of valuable hydrocarbon fractions C_{+4} of refinery flare gases reach up to 40% by mass. of the potential.

The analysis of scientific works of Kazakh scientists shows that many people were engaged in sulfur issues.

The paper shows the possibility of using sulfur as a vulcanizing agent of rubber mixtures. Thus, the authors of the work proposed one of the ways to utilize industrial sulfur in favor of production [20].

Materials and methods of research. We have proposed a method for compressing flare gas with a liquid-ring compressor, which reduces the loss of hydrocarbon fractions and hydrogen and increases the degree of purification from hydrogen sulfide (figure 1).

A special feature of the technical offer is that the process of compression of hydrogen sulfide-containing flare gas by a liquid-ring compressor is carried out in two stages: at the first stage, an amine solution is used as the working fluid, and at the second stage, the desulfurized gas is compressed with another working fluid - a hydrocarbon absorbent. The compressor of the second stage of compression is cooled and separated to obtain the lean gas, and the absorbent, which is mixed with hydrocarbon condensate and removed from the installation. The water condensate is mixed with an alkanolamine absorbent saturated with hydrogen sulfide, and removed from the installation, and the lean gas is subjected to membrane separation to produce hydrogen and fuel gas [21].

In the proposed method, compression of desulfurized gas at the second stage using a hydrocarbon absorbent as the working fluid allows the absorption of valuable hydrocarbon fractions contained in the desulfurized gas and reduction of their losses with the fuel gas. The membrane separation of the lean gas to produce hydrogen and fuel gas reduces the loss of hydrogen with the fuel gas and returns it to the production cycle and allows to obtain a fuel gas with a high volumetric calorific value.

The presence and quantity of hydrocarbon and water condensates released during compressor separation depend on the composition, temperature, and pressure of the refinery flare gases, on the flow rate and temperature of the alkanolamine and hydrocarbon absorbents, as well as on the compression pressure at each stage and the cooling temperature of the second stage compressor. Technological parameters of the process are set based on the requirements for the composition and characteristics of fuel gas and hydrogen (hydrogen-containing gas), as well as the acceptable level of losses of hydrocarbon fractions with fuel gas.

Gasoline, kerosene, diesel fuel, and any other hydrocarbon mixtures with low viscosity can be used as a hydrocarbon absorbent.

Research results. Based on the results of the pilot run and calculation studies, the technological regulations were developed for the design of the refinery's flare gas utilization unit with a capacity of 3000 nm3/h (2.4 t/h), including a compression unit based on the NAM-2500 liquid-ring compressor of the NASH company.

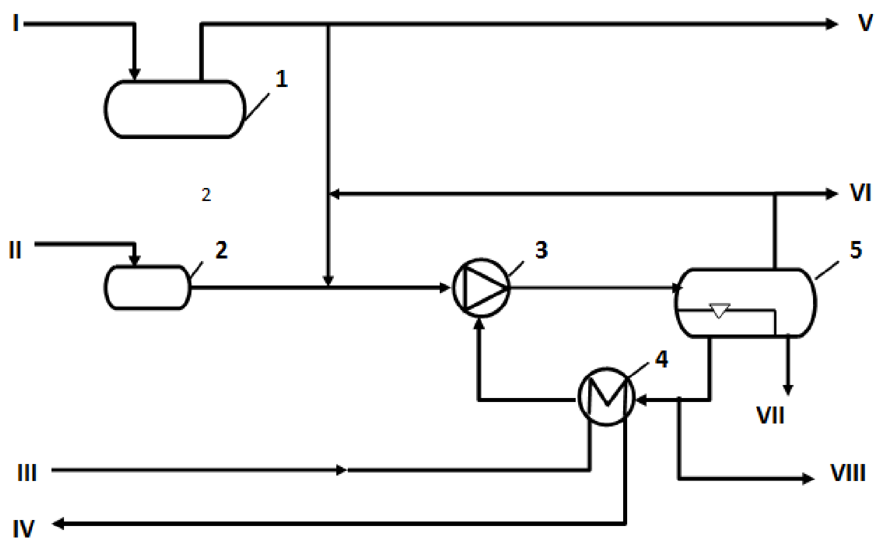

Figure 1 - The scheme of compression and purification of refinery flare gases [20]:
Flows: I – flare collector; II – fresh amine solution; III – cold coolant;
IV – hot coolant; VI – purified gas; VII – gas condensate; VIII - saturated amine solution for regeneration.
Devices: 1 – flare separator; 2 – gasoil tank; 3 – liquid-ring compressor;
4 – heat exchanger; 5 – three-phase separator.

According to the regulations, the oil refinery's flare gas, which contains 0.76% vol. of hydrogen sulfide and 45.9% vol. of hydrogen (see table 1) in the amount of 3000 nm3/h (2.4 t/h) at a temperature of 35 °C and a pressure of 0.15 MPa, is directed to the inlet of the NAM-2500 liquid-ring compressor of the NASH company. The compressor is supplied with a 15% aqueous solution of monoethanolamine in the amount of 8 m3/h as the working fluid. A compressor with a compression pressure of 0.4 MPa is sent to a separator to produce 3052 nm3/h of desulfurized wet gas containing 0.01% hydrogen sulfide and 7.99 t/h of an aqueous solution of monoethanolamine saturated with hydrogen sulfide. Hydrocarbon condensate is not released under experimental conditions, and there is no change in the hydrocarbon composition of the gas after the first stage of compression as can be seen from table 1.

Table 1 - Results of compression of flare gas with a liquid-ring compressor

No.	Components	The content of components, % vol.			
		Flare gas	Gas after the 1st compression stage	Gas after the 2nd compression stage	Fuel gas
1	Methane	25,34	24,9	27,18	44,0
2	Ethane	6	5,9	5,89	7,19
3	Propane	6,63	6,52	5,22	12,2
4	Isobutane	2,43%,	2,39	1,37	3,18
5	N-butane	3,84%	3,77	1,83	4,23
6	Isopentane	1,89	1,86	0,5	1,13
7	N-pentane	0,77	0,76	0,17	0,37
8	Propylene	2,18	2,14	1,79	4,19
9	Butylenes	0,13	0,13	0,07	0,16
10	Pentenes	0,34	0,33	0,09	0,19
11	Hydrogen sulphide	0,76	0,01	0,01	0,02
12	Nitrogen	3,77	3,71	4,11	9,66
13	Hydrogen	45,9	45,1	50,77	12,4
14	Carbon dioxide	0,02%	-	-	-
15	Water	-	2,48	1,0	1,08

Further, the desulfurized gas is sent for compression to the inlet of a liquid-ring compressor, where 8 t/h of raffinate from the aromatic hydrocarbon extraction unit is used as working fluid and compressed to 0.8 MPa. After that, the compressor is cooled to 40 °C and separated to produce 2730 nm3/h of lean gas and 8.6 t/h of absorbate, which is sent to pyrolysis, and 37.9 kg/h of water condensate, containing dissolved monoethanolamine vapor, which is mixed with an aqueous solution of monoethanolamine saturated with hydrogen sulfide and sent for regeneration. An increase in the mass of the absorbate by 0.6 t/h (8.6 t/h against the initial mass of the working fluid of raffinate, 8.0 t/h) is associated with the absorption of valuable C4+ hydrocarbon fractions contained in the initial flare gas. It allows to reduce their content in the gas, as can be seen from Table 1, and by this reduce their losses due to combustion in the fuel gas

Then, to separate the hydrogen, the lean gas is sent to a membrane gas separation unit, which produces 1.35 t/h (1160 nm3/h) of fuel gas and 0.45 t/h (1570 nm3/h) of hydrogen-containing gas with a content of 79% vol. of hydrogen. The resulting hydrogen concentrate is compressed for short-cycle adsorption (SCA) process, which produces 1240 nm3/h of pure hydrogen, as well as 330 nm3/h of fuel gas. After mixing the fuel gas from the membrane unit and the SCA, the gas is sent to the fuel network of the refinery in the amount of 1490 nm3/h, the composition of which is shown in Table 1.

Conclusions. Thus, the proposed method of gas processing can be used in the oil and gas, oil refining, and petrochemical industries for the utilization of hydrogen- and hydrogen sulfide-containing refinery flare gases. The application of the method can partially cover the demand of the oil refinery in hydrogen by reducing its losses, as well as return valuable hydrocarbon fractions to processing, and the gas purified from hydrogen sulfide - to the fuel network of the plant.

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ҚҰРАМЫНДА КҮКІРТТІ СУТЕГІ БАР ЗАУЫТТЫҚ МҰНАЙ АЛАУ ГАЗЫН КӘДЕГЕ ЖАРАТУ

Аннотация. МӨЗ-дің қазіргі заманғы алау шаруашылығы тасталатын көмірсутекті газ бен будың пайдаға асырылуын қамтамасыз ете алмайды, нәтижесінде, алау шамдарында жағылатын көмірсутекті газдың көлемі азайтылмайды және атмосфераның ластануын азайтуға мүмкіндік болмайды. Алау шаруашылығының жұмысын тұрақты және апатқа ұшырамайтындай қамтамасыз ету үшін және төгінді газды кәдеге жарату тиімділігін арттыру үшін механикалық немесе ағынды компрессорларды пайдалана отырып, оларды алдын ала компримирлеу және газ тазалау қондырғыларын салу талап етіледі.

Құрамында күкіртсутегі бар зауыттық мұнай алау газын кәдеге жаратудың аз шығынды тәсілі ұсынылды, бұл тәсілдің құрамында алканоламиннің су ерітіндісін сығудың бірінші сатысында жұмыс сұйықтығы ретінде пайдалану арқылы сұйықты-сақиналы компрессормен екі сатылы газды сығу, сондай ақ сығудың бірінші сатысы бойынша компрессатты сепарациялау арқылы күкіртсіздендірілген газ алу және көмірсутекті конденсат пен күкірт сутегімен қаныққан алканоламин абсорбентін алу қарастырылған.

Техникалық ұсыныстың негізгі ерекшелігі – құрамында күкіртсутегі бар факельді газды сұйықты-сақиналы компрессормен сығу процесі екі сатыда жүзеге асырылуында: бірінші сатыда жұмыс сұйықтығы ретінде амин ерітіндісі пайдаланылады, ал екінші сатыда күкіртсіздендірілген газды сығу басқа жұмыс сұйықтығымен, яғни, көмірсутекті абсорбент арқылы жүргізіледі.

Екінші сатыда күкіртсіздендірілген газды сығуды жұмыс сұйықтығы ретінде көмірсутекті абсорбентті пайдалану арқылы сұйық-сақиналы компрессормен жүргізеді, сығудың екінші сатысы бойынша компрессатты салқындату және сепарациялау арқылы бензинденбеген газды, су конденсатын және абсорбатты алады. Су конденсатын қаныққан күкіртсутекпен, алканоламин абсорбентімен араластырады және регенерацияға шығарады, көмірсутегі конденсатын ЖККФ-ды (жеңіл көмірсутектердің кең фракциясы) алатындай етіп абсорбатпен араластырады, ал бензинделген газ сутегі мен отын газын алу арқылы мембраналық бөлуге ұшырайды.

Компрессаттарды сепарациялау кезінде бөлінетін көмірсутекті және су конденсаттарының болуы және олардың мөлшері, зауыттық мұнай алау газдарының құрамына, температурасына және қысымына, алканоламин және көмірсутекті абсорбенттердің шығыны мен температурасына, сондай-ақ, екінші сатылы компрессаттың әрбір сатыдағы сығылу қысымынан және оның салқындату температурасына байланысты болады. Үдерістің технологиялық параметрлері отын газы мен сутегінің (құрамында сутегі бар газ) құрамы мен сипаттамаларына, сондай-ақ отын газы бар көмірсутек фракциялары шығынының рұқсат етілген деңгейіне қойылатын талаптарға сүйене отырып беріледі.

Көмірсутекті абсорбент ретінде бензиндер, керосиндер, дизель отындары және тұтқырлығы төмен кез келген басқа да көмірсутекті қоспалар пайдаланылуы мүмкін.

Тәжірибелік жүріс және есептік зерттеулер нәтижелері бойынша NASH фирмасының NAM-2500 маркалы сұйықтықты-сақиналы компрессор негізіндегі компримирлеу блогын қамтитын өнімділігі 3000 нм^3/сағ (2,4 т/сағ) МӨЗ-ның факелді газын кәдеге жарату торабын жобалауға технологиялық регламент әзірленді.

Ұсынылған әдісті қолдану МӨЗ-нің сутегідегі қажеттілігін оның шығынын азайту есебінен ішінара жабуды, сондай-ақ газды және көмірсутекті фракцияларды қайта өңдеуге немесе зауыттың отын желісіне қайтаруды қамтамасыз етуі мүмкін.

Түйін сөздер: алау қондырғысы, мұнайды қайта өңдеу; төгінді газ; күкіртті сутегі; газдарды тазарту; газдарды компримирлеу; сұйықтықты-сақиналы компрессор; сутекті кәдеге жарату; отын газы.

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УТИЛИЗАЦИЯ СЕРОВОДОРОДСОДЕРЖАЩИХ НЕФТЕЗАВОДСКИХ ФАКЕЛЬНЫХ ГАЗОВ

Аннотация. Современное факельное хозяйство НПЗ не обеспечивает полезное использование сбрасываемых углеводородных газов и паров, что не позволяет уменьшать объем сжигаемых в факельных свечах углеводородного газа и снижать загрязнение атмосферы. Для обеспечения устойчивой и безаварийной работы факельного хозяйства и для повышения эффективности утилизации сбросных газов требуется их предварительное компримирование с использованием механических или струйных компрессоров и сооружение газоочистных установок.

Предложен малозатратный способ утилизации сероводородсодержащих нефтезаводских факельных газов, включающий двухступенчатое сжатие газов жидкостно-кольцевым компрессором с использованием на первой ступени сжатия водного раствора алканоламина в качестве рабочей жидкости, сепарацию

компрессата первой ступени сжатия с получением обессеренного газа, углеводородного конденсата и насыщенного сероводородом алканоламинового абсорбента.

Особенностью технического предложения является то, что процесс сжатия сероводородсодержащего факельного газа жидкостно-кольцевым компрессором осуществляют в две ступени: на первой ступени в качестве рабочей жидкости используют аминовый раствор, на второй ступени сжатие обессеренного газа проводят другой рабочей жидкостью ─ углеводородным абсорбентом.

На второй ступени сжатие обессеренного газа проводят жидкостно-кольцевым компрессором с использованием в качестве рабочей жидкости углеводородного абсорбента, охлаждением и сепарацией компрессата второй ступени сжатия получают отбензиненный газ, водный конденсат и абсорбат. Водный конденсат смешивают с насыщенным сероводородом алканоламиновым абсорбентом и выводят на регенерацию, углеводородный конденсат смешивают с абсорбатом с получением ШФЛУ, а отбензиненный газ подвергают мембранному разделению с получением водорода и топливного газа.

Наличие и количество углеводородного и водного конденсатов, выделяемых при сепарации компрессатов, зависит от состава, температуры и давления нефтезаводских факельных газов, от расхода и температуры алканоламинового и углеводородного абсорбентов, а также от давления сжатия на каждой из ступеней и температуры охлаждения компрессата второй ступени. Технологические параметры процесса задаются исходя из требований, предъявляемых к составу и характеристикам топливного газа и водорода (водородсодержащего газа), а также к допустимому уровню потерь углеводородных фракций с топливным газом.

В качестве углеводородного абсорбента могут быть использованы бензины, керосины, дизельные топлива и любые другие углеводородные смеси с невысокой вязкостью.

По результатам опытного пробега и расчетных исследований разработан технологический регламент на проектирование узла утилизации факельного газа НПЗ производительностью 3000 нм^3/час (2,4 т/час), включающий блок компримирования на основе жидкостно-кольцевого компрессора марки NAM-2500 фирмы NASH.

Применение способа может частично покрыть потребности НПЗ в водороде за счет снижения его потерь, а также возвратить газ и углеводородные фракции на переработку или в топливную сеть завода.

Ключевые слова: факельная установка, переработка нефти; сбросный газ; сероводород; очистка газов; компримирование газов; жидкостно-кольцевой компрессор; утилизация водорода; топливный газ.

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