

ADSORPTION DEVICE TREATMENT OF ASSOCIATED PETROLEUM GAS FOR POWER GENERATION

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Abstract

Hydrocarbon resources were considered as the basis of Azerbaijan's energy security. Ensuring the most complete and rational use of oil-associated gas resources is important for improving the efficiency of the oil industry and the national economy as a whole. Associated gas from oil fields remains the least demanded hydrocarbon raw material. The perspectives for the use of oil-associated gas are associated with new directions in the technique and technology of its use as a result of the creation and implementation of mobile and stationary power plants that consume gas.

Unlike natural gas produced from gas and gas condensate fields, propane-butanoic and pentane fractions, there are hexanes, heptane's and heavy hydrocarbons, including aromatic and naphthene tic compounding. The properties of APG were studied in the laboratories. It is known that the composition of petroleum gas in a particular area, due to changes in the volume of its production on fields, is constantly changing, so it is necessary to periodically update characteristics.

The standard technology on gas conditioning for combustion is supplemented with an operation to remove heavy fractions of hydrocarbons in order to prevent these fractions from sticking to the surfaces of these installations with plugs formation and to support optimal fuel burning conditions. The problem of using oil gas in small power must be solved through new, cost-efficient developments that will be widely used both in high-output and small fields. To prepare associated oil gases for combustion, the design of an adsorption device is proposed, which makes it possible to reduce such phenomena when using this type of fuel as the formation of oil and paraffin deposits on the design details of gas burners, the accumulation of products of incomplete combustion of fuel on the heating elements of power plants. With the help of the newly proposed adsorption plant, the process of emulsifying and transporting petroleum gases has become more efficient. The use of this device has increased economic efficiency.

Keywords: gas, hydrocarbons, fuel, zeolite, fractions, natural, energetics, results, method, regeneration.

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1. Introduction

Natural hydrocarbon resources are a national patrimony. They have always been considered as the basis of energy security. However, their functions in globalization context of the world economy and the shortage of energy resources are becoming much more diverse. Particular attention should be paid to associated oil gas, the use of which for many oil companies is «unprofitable business». Ensuring the most complete and rational use of AOG resources is important for improving the efficiency of the oil industry and the national economy as a whole. Associated gas from oil fields remains not enough demanded raw hydrocarbon material. This is largely due to the remoteness of oil fields from main gas pipelines and the practice of field development that has developed in the recent past. Currently, about 3 billion m³ of AOG is extracted per year, while about 1 billion m³ is burned in torches due to the lack of other options for its use [1]. This situation forces us to consider

additional ways of efficient gas utilization directly at the place of its production. The development of new methods for increasing the collection and utilization of waste gases remains relevant, so it is important to conduct new research. For this, it is necessary to develop and apply new devices.

2. Materials and methods

Two directions of AOG use are possible (excluding useless flaring of gas phase): energy and petrochemical. The energy direction prevails due to the practically unlimited sales market and the comparative simplicity of the technological process. Oil and petrochemical – AOG can be processed to produce commercial gas that meets OST 51.40 * 93 «Fuel, natural gases supplied and transported through main gas pipelines», natural gasoline, a wide fraction of light hydrocarbons. Associated gas is a raw material for the production of methanol, formaldehyde, acetic acid, acetone and many other chemical compounds. Synthesis gas is also obtained from AOG, which is widely used for the subsequent synthesis of valuable oxygen-containing compounds – alcohols, aldehydes, ketones, acids. Oil gas serves as a raw material for the production of olefinic hydrocarbons, primarily ethylene and propylene.

In the field of AOG use, the perspectives are associated with new directions in the technique and technology of its use as a result of the creation and implementation of mobile and stationary electric power installations that consume gas. At the same time, the main requirements for AOG as a fuel follow from the technical characteristics of the field's small-scale power generation units. Knowing the physical and chemical characteristics of this fuel, it is possible to make a choice of the method of preparation of the appropriate technical means and reagents, the territorial location of preparation facilities and gas consumption, taking into account the specifics of consumers and other factors to achieve the best energy performance. Unlike natural gas produced from gas and gas condensate fields, oil gas is characterized by a high content of ethane, propane-butane and pentane fractions, hexanes, heptanes and heavy hydrocarbons, including aromatic and naphthenic compounds (benzene, toluene, xylenes, cyclopentane, cyclohexane, etc.). The content of heavy hydrocarbons (ethane and higher) in associated gases reaches 20...40, sometimes 60...80 %. Non-hydrocarbon components of AOG are represented mainly by nitrogen and carbon dioxide with an admixture of hydrogen sulfide and inert gases (mainly helium), hydrogen is sometimes found [2].

The study of individual fractions of oil and gas and the direct determination of individual hydrocarbons in them is possible using the methods of gas-liquid chromatography in combination with mass spectrometry, infrared spectroscopy and other physicochemical research methods. The laboratories studied the properties of AOG. It is known that the composition of petroleum gas in a particular area, due to changes in the volume of its production by fields, is constantly changing, so it is necessary to periodically update the indicators (at least once every 5 years). The results of the latest gas studies of three oil fields of SOCAR Azerbaijan (Gunashli, 28 May, Pirallahi) are presented in **Table 1**.

When studying APG, a research methodology was used to determine the component composition of natural and associated gases containing hydrocarbons C_1-C_6 , as well as non-hydrocarbon components (hydrogen, helium, oxygen, nitrogen, oxide and carbon dioxide).

The component composition of AOG was determined by gas adsorption chromatography in accordance with GOST 23781-87 «Combustible natural gases. Chromatographic method for determining the component composition». This standard applies to natural hydrocarbon gases and establishes two methods for the chromatographic quantitative determination of components: a method for determining nitrogen, oxygen, helium, hydrogen, carbon dioxide and C_1-C_6 hydrocarbons with a volume fraction of C_5 and higher hydrocarbons not more than 1 % and nitrogen not more than 20 %; method for determining hydrocarbons from C_4 and above (up to C_8) with a volume fraction of 0.001 to 0.5 %. The hydrocarbon part of the AOG was analyzed on a 2-meter column filled with a polymeric sorbent «parapak-Q». The non-hydrocarbon part was analyzed on a 3-meter column filled with CaA brand zeolites. Hydrocarbons C_1-C_6 and CO_2 were analyzed on a chromatograph equipped with a temperature programming unit. Heavier C_7-C_8 hydrocarbons were determined using a 50 m column filled with OV-101 stationary liquid phase using a flame ionization detector in the column temperature programming mode.

Table 1

Component composition of AOG Guneshli, 28 May, Pirallahi fields, % mol

Components	Gunashli field		28 May field		Pirallahi field	
	$P_e = 5.9 \text{ atm.},$ $T_1 = +26 \text{ }^\circ\text{C}$	$P_e = 6.2 \text{ atm.},$ $T_1 = 0 \text{ }^\circ\text{C}$	$P_e = 5.9 \text{ atm.},$ $T_1 = +26 \text{ }^\circ\text{C}$	$P_e = 6.2 \text{ atm.},$ $T_1 = 0 \text{ }^\circ\text{C}$	$P_e = 5.9 \text{ atm.},$ $T_1 = +26 \text{ }^\circ\text{C}$	$P_e = 6.2 \text{ atm.},$ $T_1 = 0 \text{ }^\circ\text{C}$
–						
oxygen	0.10	0.12	0.10	0.11	0.10	0.12
nitrogen	1.52	1.76	2.26	2.45	2.71	2.40
Carbon dioxide	0.92	1.18	0.86	1.10	0.12	0.14
methane	86.32	86.53	55.39	65.52	54.36	58.64
ethane	4.14	3.59	6.71	7.38	4.87	4.56
propane	2.83	2.45	14.79	13.11	18.64	18.03
isobutane	0.72	0.64	3.93	2.52	4.73	3.94
n-butane	1.11	0.96	8.21	4.74	9.40	9.73
pentane	0.32	0.26	2.25	1.07	1.69	1.77
n-pentane	0.32	0.24	2.18	1.00	1.83	1.55
n-hexane	0.07	0.06	–	–	0.30	0.84
heptane+high	0.08	0.07	1.59	0.79	2.89	2.14
Moisture dew point temperature, $^\circ\text{C}$	–14	–12	–13	–12	–15	–13
Hydrogen sulfide content, g/m^3	0.0007		0.0008		0.0007	
Heat of combustion, kJ/m^3	41000		54305		54702	
Water content, g/m^3	1.4		1.8		1.7	

Samples of reservoir fluids and gases were studied in specialized laboratories in accordance with the industry standard OST 153-39.2-048-2003 «Oil. Model studies of reservoir fluids and operated oils». The heat of combustion is the main characteristic in assessing the energy intensity of AOG. According to GOST 22667-82, the calorific value is determined by additivity using data on the composition and corresponding calorific values of natural gas components. Accounting for the calorific value and chloride equivalent of AOG when it is consumed as a fuel for small-scale power generation is of no small importance, since underestimation of these indicators can lead to unjustified gas losses, and their overestimation can cause complications in providing consumers with fuel. Gunashli gas of the oil field has a fairly high calorific value – about 41.000 kJ/m, for 28 May – 54.305 kJ/m, for Pirallahi – 54.702 kJ/m, which is compared with natural gas, the calorific value of which for most fields is 35.500 kJ/m...37560 kJ/m, is a fairly significant factor [3, 4].

Depending on the quality of the produced AOG, gas conditioning of varying degrees of complexity is required. One of the most serious problems in the use of oil gas is its purification from gas condensate, drip, fine, aerosol moisture and mechanical sludge impurities. According to the data on the composition of the gas (**Table 1**), the following requirements for operations for the preparation of AOG for small-scale power generation are substantiated:

1. Before entering the gas supply system to the power plant, AOG must be maximally separated from impurities and dehydrated to prevent the formation of crystalline hydrates during gas supply. Permissible value of moisture is not more than 9 mg/Nm³ [1].

2. Purification of gas from hydrogen sulfide and carbon dioxide should be used to remove them in order to prevent their corrosive effect on equipment and pipeline communications and bring their content in the gas in line with the requirements of sanitary standards. The content of sulfur compounds (in terms of sulfur) in the AOG supplied to the gas engine (in the case of stationary gas generating sets) should not exceed 0.2 % (by mass).

3. Gas stripping (full or partial) is used to remove propane-butane and heavier hydrocarbon components from gas in order to prevent the formation of liquid locks.

4. Each gas fraction has its own ignition temperature, therefore, an unstable gas combustion mode (detonation mode) appears, which is determined by the minimum allowable methane number; to increase the methane number and prevent detonation phenomena during combustion,

various gas treatment methods are used, including the aforementioned removal of individual heavy hydrocarbon components of the gas. Thus, an operation to remove heavy fractions of hydrocarbons is added to the standard technology for preparing gas for combustion in order to prevent these fractions from sticking to the surface of these installations with the formation of plugs and to maintain optimal conditions for fuel combustion. Despite the existing capital-intensive and multi-stage technologies for the preparation of oil gas for use in small power generation, the issue of preparation should be resolved in favor of low-cost, but efficient installations.

Combustion of oil gas containing an insignificant amount of hydrocarbon components as a fuel in field conditions on the simplest gas burner units, as a rule, occurs in a detonating mode with low efficiency, is accompanied by incomplete gas combustion and a significant emission of pollutants into the atmosphere [5, 6]. As a solution to this problem, the use of adsorption devices with zeolite filler as an element of pre-burner preparation of fuel is considered. The process of adsorption is known and widely used in the oil industry. It is possible to calculate the adsorption rate, saturation time, however, in the case when a gas, such as APG, has a complex chemical composition that varies with time and depending on the ambient temperature, only data obtained directly during the experiment in natural conditions can be reliable.

The objective of the field experiment is to test the efficiency of the zeolite filter as an upstream adsorption device during AOG compression in power plants directly at the production site. The technique for studying the effectiveness of an adsorption device consists in determining the operational life of a zeolite filter depending on the number of regenerations and the operating time according to the well-known scheme [1, 2]. A cogeneration plant from CATERPILLAR (USA) was adopted as a pilot plant, hereinafter referred to as a power plant (PP), designed for autonomous production of its own electricity. The main components of the power plant are a 4-stroke internal combustion engine running on gaseous fuel and a generator set. Before the power plant, the gas passes through the gas distribution point, where the gas undergoes primary cleaning through the strainer and regulated to the operating pressure. At the inlet to the power plant, before and after the filter element, there are pressure gauges to determine the pressure drop. Next, according to the scheme, there is a purge plug, a vortex gas meter for determining gas flow, shut-off valves [7]. Structural and operational ratings of the power plant: installation type CAT G3516, gas flow rate 274 m³/h. In accordance with the task of the experiment, the power plant is equipped with an adsorption device, which is installed as a stage of additional gas purification after a standard filter, which is part of the gas control device (**Fig. 1**). The adsorbing component – zeolite, in this case, chabazite, was chosen based on the study of adsorption equilibria, energy and adsorption under given conditions. The constructive calculation of the adsorption device was carried out kinetics of dehydrated chabazite [8].

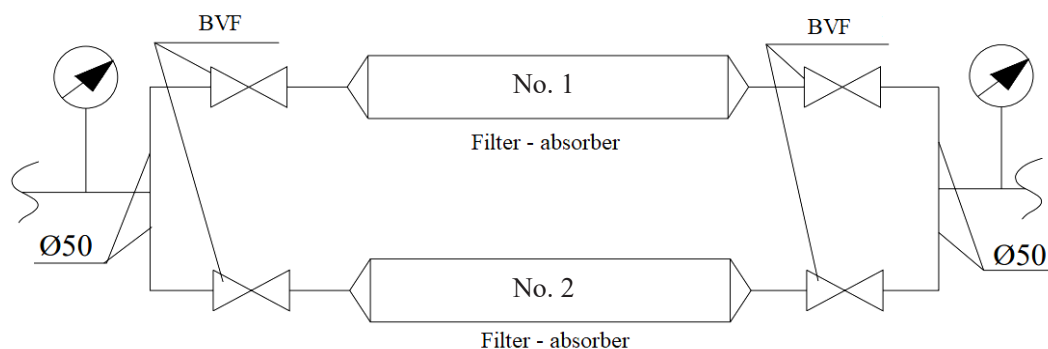


Fig. 1. Connection diagram of insert with adsorption device BVF – Ball Valve Faucet

The adsorption device will make it possible to purify the gas from heavy hydrocarbons, dry and «smooth out» fluctuations in the composition of the gas associated with changes in ambient temperature. The mass of the zeolite is 49.46 kg. The adsorption device was manufactured at the AzXIMMASH (chemical engineering plant) plant in Baku. The regeneration of the adsorption

device was carried out by blowing it with hot air with a temperature of up to 400 °C at a zeolite regeneration plant.

3. Results and discussion

The results of the operation of the adsorption device were evaluated by the characteristic of the pressure drop according to the readings of the installed pressure gauges and by the chemical analysis of samples taken through the fuel supply purge plugs and the power plant before and after the filter [9, 10].

The component composition of AOG was determined by gas adsorption chromatography on a Kristall-2000 M chromatograph. The duration of the experiment was 84 days (the interval of the regulations for the next maintenance of the power plant), which makes it possible to judge the operation of the zeolite filter in off-season conditions and at the required loads.

The curves are based on the results of the survey of oil fields and the results of experiments. The effect of the adsorbent used as a function of time is shown here.

The results of the experiment on the full-scale study of the adsorption device are presented in the graphs (Fig. 2).

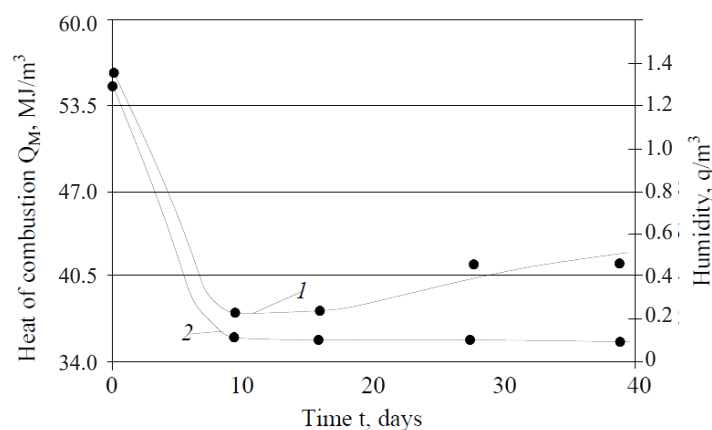


Fig. 2. Change in lower combustion heat (1) and moisture content (2) during the use of an adsorption device

According to the results of laboratory analyzes on the chemical composition of AOG, it can be judged that the use of adsorbents based on chabazite allows to reduce the content of heavy hydrocarbons and thereby increase the overhaul period during the operation of power equipment (Table 2). Thanks to the performance characteristics obtained, it is possible to determine the saturation time of the zeolite under given conditions without regeneration until the maximum pressure drop is reached – it is about 10.6 hours. During the operation of the adsorption device, it was noted that the periodically repeated regeneration process negatively affects the ability of the zeolite to absorb. The maximum value of the number of regenerations to maintain the optimal value of the pressure drop before and after the adsorption device according to the specifications EU-97 times. If the necessary measures are taken to control the composition of the purified gas and the pressure gauge readings, it becomes possible to optimally improve the AOG flaring process in the power plant.

Collection, preparation, transportation and processing of AOG have their own technological and economic features and problems, which differ to a large extent from the technology and economic parameters of production, treatment and transportation of natural gas. The situation with energy supply that has developed in the fields prompts us to consider the possibility of using AOG for our own needs as fuel for small power plants. The use of AOG in this capacity is usually accompanied by complications: the formation of hydrate and liquid plugs in the supply gas pipelines, periodic flooding of gas burner units, which can initiate explosive equipment. In most cases, condensate that falls in field gas pipelines and is collected in condensate collectors is thrown

into pits for evaporation and incineration. Combustion of oil gas containing a significant amount of hydrocarbon components as a fuel in field conditions on the simplest gas burners occurs in a detonating mode with low efficiency, is accompanied by incomplete combustion of gas and a significant emission of pollutants into the atmosphere.

Table 2

Experiment results on the full-scale study of the adsorption device

Defined component, properties	el. dim.	Analysis results				
		Before the start of the experiment	225 h	384 h	662 h	934 h
Carbon dioxide		0.032	0.037	0.035	0.035	0.036
Nitrogen		3.485	3.962	3.960	3.961	3.962
Methane		66.104	74.749	74.652	74.737	74.740
Ethane		3.567	4.039	4.021	4.037	4.038
Propane		14.324	14.309	14.307	14.315	14.308
Isobutene	% volume	3.040	0.982	0.988	0.986	0.981
n-butane		6.782	1.745	1.876	1.755	1.757
Isopentane		1.096	0.098	0.107	0.096	0.097
n-pentane		1.141	0.059	0.073	0.055	0.054
Sum of hexanes		0.388	0.011	0.014	0.012	0.013
Amount of heptanes		0.041	0.009	0.017	0.011	0.014
absolute density at 20 °C and 101.325 kPa	kg/m ³	1.111	0.188	0.193	0.203	0.205
absolute density	–	0.922	0.124	0.247	0.264	0.273
Low combustion temperature at 20 °C and 101.325 kPa	kJ/m ³	55860	37475	37685	41401	41476
Hydrogen sulfide content	q/m ³	<0.001	<0.001	<0.001	<0.001	<0.001
Water content	q/m ³	1.3	0.1	0.1	0.1	0.1

Periodically repeated regeneration process negatively affects the absorption capacity of the zeolite. The maximum value of the number of regenerations to maintain the optimal value of the pressure dropping before and after the adsorption device is about 100 times.

The saturation time of the zeolite without regeneration is 10.6 h until reaching the maximum pressure drop.

4. Conclusion

A new adsorption unit was developed. The regeneration of zeolite used in this unit is carried out in mining conditions. The efficiency of using gas and petroleum gases in small power generation increases. The use of the newly developed unit in the oil industry will lead to high performance. A high degree of results will be obtained in the purification of gases. After the use of the new facility, it will be possible to clean energy gases according to high standards.

The use of these devices in the oil industry will lead to the achievement of high economic efficiency.

Conflict of interest

The authors declare that they have no conflict of interest in relation to this research, whether financial, personal, authorship or otherwise, that could affect the research and its results presented in this paper.

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Data availability

Manuscript has no associated data.

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