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Prospects for the Use of Associated Gas of Oil Development as Energy Product

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ABSTRACT

The paper analyzes the scope of associated petroleum gas (APG) losses and estimates the emissions of harmful substances into the atmosphere when APG is burned in flare devices. The technique of industrial monitoring of atmosphere air for industrial facilities of oil development is proposed. The purpose of this work is to create industrial systems for using the resource and energy potential of associated gas of oil development while minimizing a negative impact on the environment under the terms of self-repayment.

Keywords: Emissions of Harmful Substances, Oil and Gas Separation, Absorption Drying, Mono-ethanolamine, Atmospheric Air Pollution Monitoring
JEL Classifications: Q34, Q43, Q52, Q53

1. INTRODUCTION

The industrial practice gives evidence of large-scale negative consequences associated with the uncontrolled pollution of the atmosphere with associated gas of oil development and oil products as a result of flare devices operation (Korzhubaev, 2009; Korzhubaev, 2012; Hughes, 2013). The index of flaring (deflation) of associated petroleum gas (APG) in flare devices should not exceed 5% of the volume of the produced associated gas. In order to achieve this result, it is necessary to introduce systems for its targeted use that will significantly reduce emissions of harmful substances into the atmosphere. It should be noted that the absolute volumes of APG and combustion gases are quite big. According to various estimates, they can amount to 10-11 billion m^3 per year. Therefore, it can be argued that the use of APG is economically and environmentally appropriate (Korzhubaev, 2009; Korzhubaev, 2012; Hughes, 2013; Aksenov, 2016; Krivov, 2013; Korzhubaev, 2012).

Recommended measures to improve associated gas utilization technologies assume the following cycle of operations:

- Gathering and processing system management of APG for supply to would-be customers;
- Gathering and compressing APG with subsequent injection into compressed cylinders in order to provide industrial facilities with an energy source for internal needs (heat supply, hot water supply, maintenance of the technological process).

We should consider in parallel the possibility of implementing modern technologies for demineralization of oilfield water and its use in recycling water supply or alternative technologies to maintain the reservoir pressure in oil development.

The main types of man-caused impacts in oil development given in Table 1 are related to boreholes drilling, construction and assembling operations carried out within the areas allocated for producing wells, arrangement of processing areas and line facilities, and the installation of oil-storage pits. At the same time, there is a serious possibility that oil products and polluting substances enter the environment as a result of implementation of auxiliary processes and separate operations.

The main factors influencing the environment during the development of oil fields are the operational emission of combustion gases in flare devices of the central processing facility, as well as exhaust gases from diesel engines of drilling units. Other

Table 1: Impact of oil production facilities on components of the environment (Korzhubaev, 2009; Aksenov, 2016; Krivov, 2013; Eder, 2016; Stern, 2006; Flanner et al., 2007; Sims, 2008)

Component of the environment	Source of impact	Characteristic of impact
Atmosphere	Flange coupling of oil pipelines, shutoff and control valves, pumps, pressure vent valve, etc.; Oil traps; Oil based fluid pouring into oil tankers	Emissions of hydrocarbons into the atmosphere
	Flare devices	Nitrogen oxide, nitrogen dioxide
	Machinery and equipment	Carbon monoxide, sulfur dioxide, pure carbon black, benzpyrene, hydrogen sulphide, methane
Hydrosphere	Drilling operations	Crude oil and refined products
	Orchestrated water course (refinery water)	Highly mineralized oilfield water
	Unorchestrated water course (overland flow); Disturbance situations	Chemical agent, synthetic surface active substance, suspended matters
Rock sphere	Boreholes drilling;	Landscape change;
	Formation of excavated material	Destruction, soil contamination
	Leakage and oil spillage	Soil contamination with oil products and chemicals; Soil salinization
Bioenvironment	Contaminated soils	Depletion in numbers and group composition of mesofauna
	Contaminated water	Direct impact on the epidermis of animals; Toxic and narcotic action of paraffin hydrocarbons

factors influence in smaller quantities such as evaporation of light hydrocarbon fractions with leakage of equipment, spillages on the ground of well-bore fluids, oilfield and refinery water, treated oil, reactants followed by percolation into the cenozoic water-bearing horizons and drainage along the lower areas towards the surface and permanent watercourses (Korzhubaev, 2009; Aksenov, 2016; Krivov, 2013; Eder, 2016; Stern, 2006; Flanner et al., 2007; Sims, 2008).

2. METHODS

Initial treatment (processing) of oil in oil pumping plants (OPF) is its dehydration and desalination in order to reduce ballast (water) during transportation, as well as degassing to reduce the vapor pressure. The scheme of the oil and gas separation process is shown in Figure 1.

There are mechanical, thermo-chemical and electrochemical methods of demulsification in industrial practice. The mechanical method of demulsification is carried out according to a two-stage scheme in the sludge tanks of Stages I and II. When implementing the process of chemical demulsification, industrial demulsifiers are used, the supply and dosage of chemical agents to which is produced in package plants. Dehydration and desalting of oil are carried out in field-assisted electric dehydrators.

It can be seen from the scheme that in order to ensure oil and gas separation an excessive heat supply is needed for demulsification processes; fresh water is needed for desalination.

The characteristics of intermediate stocks (Table 2) make it possible, if necessary, to determine the volume of APG, set the conditional productivity and predict the capacity of the gas-fired supply system.

3. RESULTS

Based on the initial characteristics of raw materials and volumes of oil produced, it is possible to determine the volume of APG produced by the enterprise. Table 3 shows the characteristics of a typical composition of raw feedstock. Table 4 gives an approximate component composition of APG and its main properties.

Let us calculate the emissions of harmful substances into the atmosphere as a result of the combustion of APG.

The conditional daily production rate of the enterprise is 1200-1300 tons. According to the gas-oil ratio, it is possible to determine the total volume of produced oil gas per day by specifying the conditional productivity:

$$V = Q \cdot q_T = 1249 \cdot 10.85 = 135{,}551.65\ \text{m}^3/\text{day} \qquad (1)$$

Where, Q – Conditional daily oil production, t/day;

q_T – Amount of oil gas per ton of oil produced, t/day.

APG emissions are calculated using the methodology for calculating emissions of harmful substances into the atmosphere when flaring APG in flare devices in accordance with applicable standards and regulations ("On Approval of the Methodology for Calculating Emissions of Harmful Substances into the Atmosphere during the Flaring of Associated Petroleum Gas at Flare Devices." Order of the State Committee for Ecology of Russia No. 199, 1998).

Based on the initial data of the component composition of APG, we determine the molecular weight of each component and calculate the mass fraction. For ideal gases, the numerical values of the molar and volume fractions are the same.

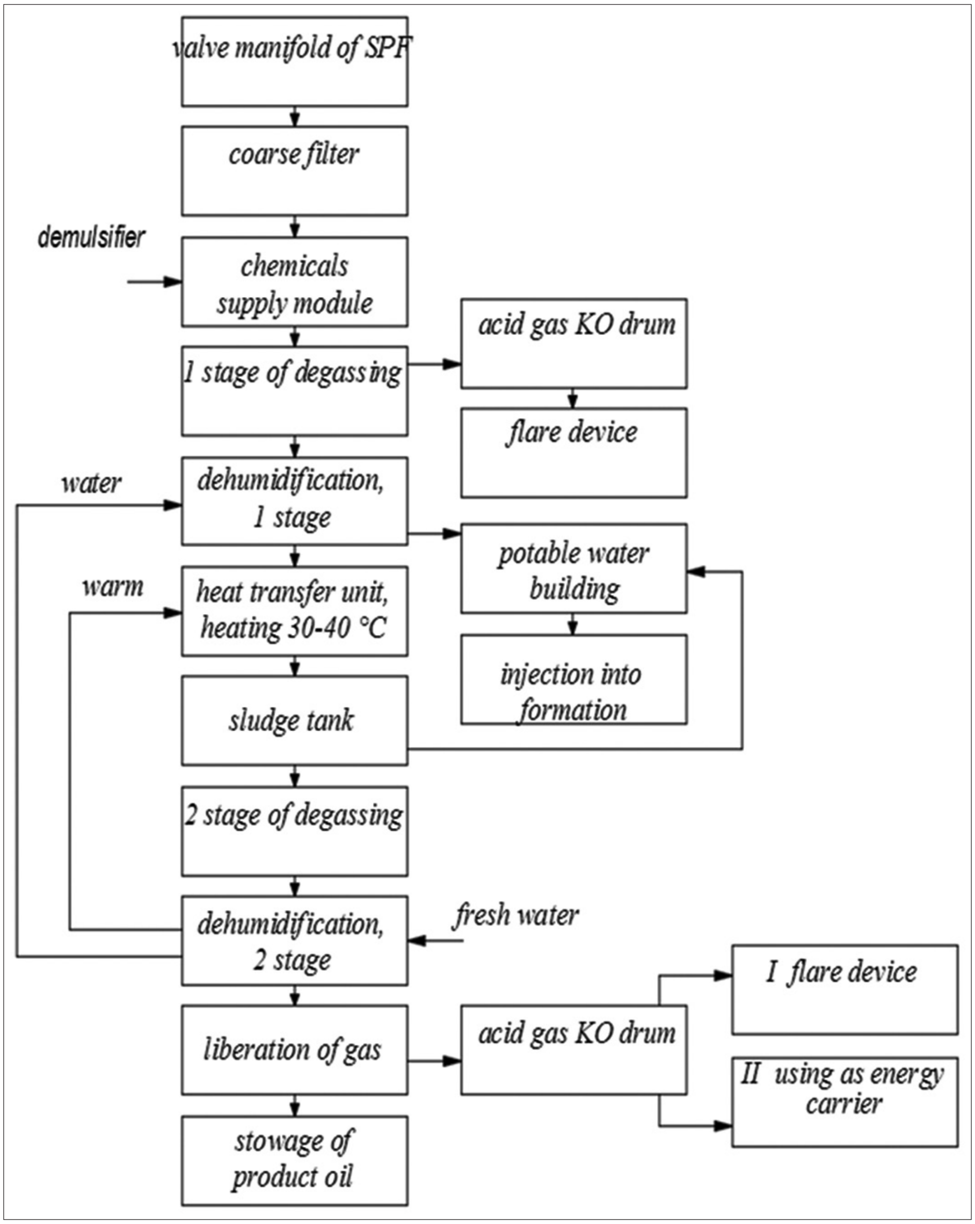


Figure 1: An approximate scheme of oil and gas separation (Solovyanov, et. al. 2013; Kirillov 2014; Pyatibratov 2014)

Table 2: Characteristics of intermediate stocks (Solovyanov et al., 2013; Ferencz, 2012; Leontev, 2012)

Name of intermediate stocks	Quality drivers required for verification	Rate as received
Dehydrated oil	Water content, %	0.3
	Density, g/cm^3	0.9260
	Viscosity, MPa	208.92
	Content of chloride salts, mg/dm^3	50
Oilfield water	Density, g/cm^3	1.128
	Basic sediment, %	0.0216
	Ion composition of water, g/L	
	Cl^-	378.82
	HCO^{-3}	0.15
	Ca^{2+}	12.63
	Mg^{2+}	11.43
	Na^++K^+	209.62
	Oil products content, mg/dm^3	45
	Content of chloride salts, mg/dm^3	168,573

The formula for calculating the mass fraction is:

$$\omega_i = \frac{\chi_i \cdot M_i}{\sum_{k=1}^{14} \chi_k \cdot M_k} = \frac{\chi_i \cdot M_i}{39.8}, \qquad (2)$$

Where χ – molar fraction;
M – molecular weight.

The design data of APG:

- Mass flow: W_g = 835.9 kg/h;
- Volume flow rate: W_v = 469.6 m/h = 0.13 m/s;
- Density at standard conditions: ρ = 1.78 kg/m^3;
- Molar mass: 39.8 kg/kmol.

Let us recalculate the entire component composition into mass fractions taking into account the formula (2), and determine the mass flow of the components (Table 5).

The flare stack is a pipe with a passage diameter of 500 mm, and a height of 27.5 m/s.

Let us determine the exit velocity:

$$\upsilon = \frac{W_v}{S} = \frac{W_v}{\pi r^2} = \frac{0.13}{3.14 \cdot 0.25^2} = 0.663\,\text{m/s} \tag{3}$$

Table 3: Typical raw feedstock composition (Krivov, 2013; Pavlov et al., 1987)

Name of raw feedstock products	Quality drivers required for verification	Rate as received
Oil-in-place	Water content, %	78-80
	Density, g/cm³	1.0875
	Viscosity, MPa	66.5
	Content of chlorides, mg/dm³	157,152
	Basic sediment, %	0.0550
	Sulphur content, %	2.16
	Gas-oil ratio at 20°C, m³/t	10.85
Oilfield water	Density, g/cm³	1.145
	Exponent of hydrogen ion activity, pH	6.3-6.5
	HCO^{-3}	0.045-0.052
	Ca^{2+}	14.1-14.5
	Mg^{2+}	4.8-4.99
	$Na^{+}+K^{+}$	114-115

Table 4: Approximate component composition of associated petroleum gas and its properties (averaged data) (Korzhubaev, 2012; Krivov, 2013; Sviridova, 2015; Churakaev, 1983)

Component/ parameter	Content, %/value	Component	Content, %
Mass flow, kg/h	830.0-835.9	$i\text{-}C_4H_{10}$	2.89-3.73
Density at standard conditions, kg/m³	1.75-1.78	$n\text{-}C_4H_{10}$	8.11-8.35
Molar mass, kg/kmol	39.8	$i\text{-}C_5H_{12}$	2.98-3.55
CO_2	0.8-1.59	$n\text{-}C_5H_{12}$	2.01-2.56
H_2S	0.35-0.54	$n\text{-}C_6H_{14}$	1.80-2.32
N_2	5.89-6.67	$n\text{-}C_7H_{16}$	0.48-0.65
CH_4	6.13-6.92	$n\text{-}C_8H_{18}$	0.14-0.17
C_2H_6	32.16-34.21	H_2O	4.6-5.1
C_3H_8	21.8-23.6		

The stoichiometric reaction of combustion is written as:

$$C_cH_hS_sN_nO_o + MO_{Ko}N_{Kn}H_{Kn} = n_{CO_2}CO_2 + n_{H_2O}H_2O + n_{SO_2}SO_2 + n_{N_2}N_2 \tag{4}$$

The volume flow rate of combustion products:

$$W'_v = W_v \cdot V_{cp}\frac{(273 + T_a)}{273}, \tag{5}$$

Where, V_{cp} – the amount of combustion products formed during stoichiometric combustion of 1 m³ of APG in a humid air atmosphere, (m³/m³) which can be determined by the formula:

$$V_{cp} = C + S + 0.5\,(H + N + M \cdot (K_h + K_n)) \tag{6}$$

Where, C, S, H, N and K_h, K_n correspond to the conditional molecular formulas of APG and moist air, respectively.

The mass content of the jth chemical element in APG ω_j (wt%) is calculated according to the formula:

$$\omega_j = \sum_i \omega_i \cdot \omega_{ij}, \tag{7}$$

Where, ω_{ij} – the content (wt%) of chemical element in the ith component of APG;

ω_i – the mass content of the ith component in APG ("On Approval of the Methodology for Calculating Emissions of Harmful Substances into the Atmosphere during the Flaring of APG at Flare Devices." Order of the State Committee for Ecology of Russia No. 199, 1998).

The calculated mass contents of elements in APG are presented in Table 6.

The number of atoms of the jth element K_j (Table 7) in the conditional molecular formula of the associated gas is calculated by the formula:

$$K_j = 0.01 \cdot \frac{\omega_j}{M_j} \cdot M_A, \tag{8}$$

Table 5: Recalculation of the component composition into mass fractions

Fractional analysis, %	Molar mass, g/mol	Mass fraction, %	Mass flow of the component, kg/h	Concentration, g/m³
CO_2-1.59	44.01	1.76	14.70	31.30
H_2S - 0.54	34.08	0.46	3.87	8.23
N_2-6.67	28.01	4.69	39.24	83.57
CH_4-6.92	16.04	2.79	23.31	49.64
C_2H_6-34.21	30.07	25.85	216.05	460.07
C_3H_8-23.6	44.1	26.15	218.59	465.47
$i\text{-}C_4H_{10}$-3.73	58.12	5.45	45.53	96.96
$n\text{-}C_4H_{10}$-8.35	58.12	12.19	101.93	217.04
$i\text{-}C_5H_{12}$-3.55	72.15	6.44	53.79	114.55
$n\text{-}C_5H_{12}$-2.56	72.15	4.64	38.79	82.61
$n\text{-}C_6H_{14}$-2.32	86.17	5.02	41.99	89.41
$n\text{-}C_7H_{16}$-0.65	100.21	1.64	13.68	29.13
$n\text{-}C_8H_{18}$-0.17	114.23	0.49	4.08	8.68
H_2O - 5.1	18.02	2.31	19.30	41.10
99.96	99.87		Total C_3H_8+	1,144.95

Table 6: Mass content of elements in APG

Fractional analysis		Content of chemical elements in components (reference data)					The mass content of elements in APG				
Component	Mass fraction, %	C	H	S	N	O	C	H	S	N	O
CO_2	0.02	27.29	-	-	-	72.71	0.0048	-	-	-	0.0128
H_2S	0.0046	-	5.92	94.08	-	-	-	0.0003	0.0044	-	-
N_2	0.05	-	-	-	-	-	-	-	-	0.0469	-
CH_4	0.03	74.87	-	-	-	-	0.0209	0.0070	-	-	-
C_2H_6	0.26	79.89	20.11	-	-	-	0.2065	0.0520	-	-	-
C_3H_8	0.26	81.71	18.29	-	-	-	0.2137	0.0478	-	-	-
i-C_4H_{10}	0.05	82.66	17.34	-	-	-	0.0450	0.0094	-	-	-
n-C_4H_{10}	0.12	82.66	17.34	-	-	-	0.1008	0.0211	-	-	-
i-C_5H_{12}	0.06	83.23	16.75	-	-	-	0.0536	0.0108	-	-	-
n-C_5H_{12}	0.05	83.24	16.76	-	-	-	0.0386	0.0078	-	-	-
n-C_6H_{14}	0.05	83.73	16.27	-	-	-	0.0421	0.0082	-	-	-
n-C_7H_{16}	0.02	84.01	15.99	-	-	-	0.0137	0.0026	-	-	-
n-C_8H_{18}	0.00	84.12	15.88	-	-	-	0.0041	0.0008	-	-	-
H_2O	0.02	-	11.19	-	-	88.81	-	0.0026	-	-	0.0205
	99.87						0.7438	0.1704	0.0044	0.0469	0.0333

APG: Associated petroleum gas

Table 7: Number of atoms of the jth element

Element	M_j	K_j	Element	M_j	K_j
C	12.011	2.465	N	14.008	0.133
H	1.008	6.727	O	16	0.083
S	32.066	0.005			

The conditional molecular formula of APG is as follows:

$$C_{2.465}H_{6.727}S_{0.005}N_{0.133}O_{0.083} \tag{9}$$

At the air humidity of 60% and 20°C, the moisture content d = 0.01 kg/kg.

Then the number of atoms of chemical elements in the conditional molecular formula of moist air can be determined according to the formulas given in Table 8.

The molecular formula of moist air is as follows:

$$O_{0.433}N_{1.570}H_{0.032} \tag{10}$$

The stoichiometric reaction of combustion taking into account the performed calculations:

$$C_{2.465}H_{6.727}S_{0.005}N_{0.133}O_{0.083}+MO_{0.433}N_{1.570}H_{0.032} = n_{CO_2}CO_2+n_{H_2O}H_2O+n_{SO_2}SO_2+n_{N_2}N_2 \tag{11}$$

M is the molar stoichiometric coefficient according to the condition of the complete saturation of the valency (the complete oxidation reaction); it is calculated by the following formula:

$$M = -\frac{\sum_j k_j \cdot v_j}{\sum_j k'_j \cdot v'_j} = \frac{-4\cdot 2.465 - 1\cdot 6.727 - 2\cdot 0.005 + 2\cdot 0.083}{2\cdot 0.433 - 1\cdot 0.032} = 19.709, \tag{12}$$

Where v_j' and v_j – Valency of the elements j and j' which are the part of humid air and APG;

k_j' and k_j – number of atoms of elements in the conditional molecular formulas of moist air and gas.

The theoretical amount of moist air required for complete combustion of 1 m³ of APG is 19.709 m³. Let us determine the amount of separate combustion products:

$$n_{CO_2} = C = 2.465 \tag{13}$$

$$n_{H_2O} = 0.5 \cdot (H + MK_h) = 0.5 \cdot (6.727 + 19.709 \cdot 0.032) = 3.679 \tag{14}$$

$$n_{SO_2} = S = 0.005 \tag{15}$$

$$n_{N_2} = 0.5\ (N + MK_n) = 0.5\ (0.133 + 19.709 \cdot 1.570) = 15.538 \tag{16}$$

Hence the amount of combustion products formed during the stoichiometric combustion of 1 m³ of APG in an atmosphere of moist air:

$$V_{cp} = 2.456 + 0.005 + 0.5\ (6.727 + 0.133 + 19.709\ (0.032 + 1.570)) = 21.678\ m^3/m^3 \tag{17}$$

The specific permissible discharge of carbon dioxide is calculated by the formula:

$$q_{CO_2} = M_{CO_2} \cdot \left(\frac{c}{M_g} - \frac{q_{CH_4}}{M_{CH_4}} - \frac{q_{CO}}{M_{CO}}\right) = 44.011 \cdot \left(\frac{2.465}{39.8} - \frac{5\cdot 10^{-4}}{16.043} - \frac{2\cdot 10^{-2}}{28.011}\right) = 2.693 \tag{18}$$

The specific permissible discharge of water vapor:

$$q_{H_2O} = 0.5 \cdot M_{H_2O} \cdot \left(\frac{(h - MK_h)}{M_g} - \frac{q_{CH_4}}{M_{CH_4}}\right) = 0.5 \cdot 18.016 \cdot \left(\frac{(6.727 + 19.709 \cdot 0.032)}{39.8} - \frac{5\cdot 10^{-4}}{16.043}\right) = 1.665 \tag{19}$$

The specific permissible discharge of nitrogen:

$$q_{N_2} = M_N \cdot \left(\frac{(n + MK_h)}{M_g} - \frac{q_{NO_2}}{M_{NO_2}} \right) =$$

$$28.016 \cdot \left(\frac{(0.133 + 19.709 \cdot 1.570)}{39.8} - \frac{3 \cdot 10^{-3}}{30.008} \right) = 21.872 \qquad (20)$$

The specific permissible discharge of sulfur dioxide:

$$q_{SO_2} = M_{CO_2} \cdot \frac{S}{M_g} = 64.054 \cdot \frac{0.005}{39.8} = 0.008 \qquad (21)$$

Based on the analysis of the gas flow, the coefficient of underburning $k_u = 0.0006$.

The specific permissible discharge of hydrocarbons (on conversion to methane), as well as the sulfur compounds contained in gas such as hydrogen sulphide and mercaptan, are determined by the general formula:

$$q_{C_xH_y} = 0.01 \cdot k_u \cdot \omega_{C_xH_y} \qquad (22)$$

The emissions of hydrocarbons (on conversion to methane):

$$\omega_{(\Sigma CH_4)} = \sum \omega_i \cdot M_i / M_{CH_4} = 277 \qquad (23)$$

$$q_{CH_4} = 0.01 \cdot 0.0006 \cdot 277 = 0.001662 \text{ kg/kg} \qquad (24)$$

$$M_{CH_4} = 0.278 \cdot 0.001662 \cdot 835.9 = 0.386 \text{ g/s} \qquad (25)$$

The mass content of hydrogen sulfide is 0.46%. Then:

$$q_{H_2S} = 0.0006 \cdot 0.01 \cdot 0.046 = 0.00000276 \text{ kg/kg} \qquad (26)$$

$$M_{H_2S} = 0.278 \cdot 0.00000276 \cdot 835.9 = 0.000641 \text{ g/s} \qquad (27)$$

Let us determine the maximum emissions of harmful substances (g/s):

$$Q_{gi} = 0.278 \cdot q_i \cdot W_g \qquad (28)$$

Table 8: Number of atoms of the jth element of moist air

Element	O	N	H
K_j	(0.421+1.607d) (1+d)	1.586 (1+d)	3.215d (1+d)

The calculated values of the maximum and total emissions of harmful substances into the atmosphere during the combustion of APG are given in Table 9.

4. DISCUSSION

Transportation of oil gas is impossible for long distances because water vapor and heavy hydrocarbons condense when the temperature decreases because they form liquid, ice and hydrate plugs. Proceeding from this, the processing of this gas should be carried out in an industrial complex designed for oil and gas separation of oil-in-place.

The technological cycle assumes the following stages of processing:

- Compression;
- Drying;
- Stripping;
- Acid gas removal (Churakaev 1983; Kochi, 2013).

When these operations are over, the dried and stripped gas can be transported under high pressure for long distances. Liquefied gases are formed from unstable gasoline gas in the form of a propane-butane mixture or technically pure separate hydrocarbons and gasoline.

Liquefied gases are widely used as raw materials for the petrochemical industry; they are used as motor fuel, as well as household fuel for gasification of settlements, enterprises, livestock farms, etc.

The main consumer of liquefied gases is petrochemical production. Ethane, propane, n-butane, as well as gasoline and hexane, serve as raw materials for the production of ethylene which in turn produces ethyl alcohol, glycerin, ethylene glycol, dichloroethane, ethyl chloride, etc. Further processing of these substances gives varnishes, solvents, dyes, detergents, synthetic rubber, polyethylene, and polypropylene.

Butane is used to produce synthetic butadiene rubber; isobutane and isopentane are used for the production of isoprene rubber which is close to natural. Gasoline is used in oil refineries (oil refinery plant) as a compounding additive that improves the properties of gasoline. Liquefied gases, due to the ability to be in

Table 9: Results of calculations of emissions of harmful substances into the atmosphere during the combustion of associated petroleum gas

Substance	Specific permissible discharge at sootless flaring, kg/kg	Maximum emission of harmful substances, g/s	Gross emissions of harmful substances, g/t
CO	2×10^{-2}	4.647	146.55
N_2	3×10^{-3}	0.697	21.98
Benzo (a) pyrene	2×10^{-2}	0.464×10^{-8}	1.46×10^{-7}
SO_2	0.008	1.859	58.63
CO_2	2.693	625.80	19735.23
H_2S	$2.76\cdot10^{-6}$	0.000641	0.02
CH_4	$1.662\cdot10^{-3}$	0.386	12.17

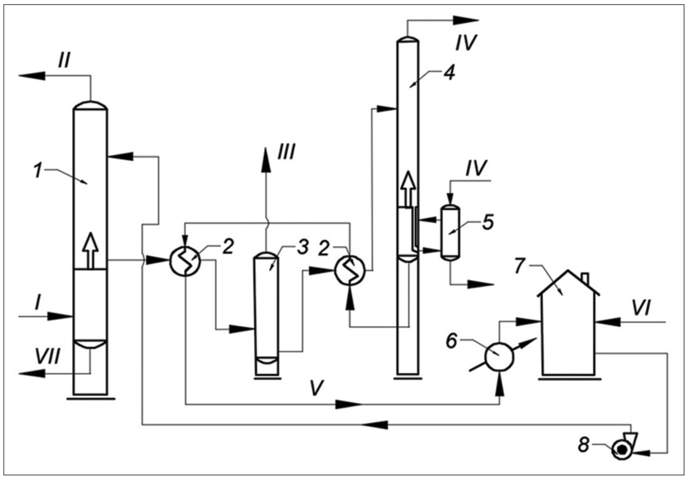
a gaseous state under normal conditions and to switch to a liquid state at relatively low excess pressures, are very convenient for the use as a household fuel. A complicated pipeline network is not required for their transportation; they can be delivered to certain areas in cylinders and special tanks. Liquefied gases are widely used for cutting metals (Churakaev, 1983; Kochi, 2013).

Thus, dried and stripped APG can be used at power plants that allow reducing emissions into the atmosphere, especially when switching from solid or liquid fuel to gas. The produced gas can also be transported to nearby industrial facilities. The part of the processed gas can be sent for sale to petrochemical enterprises and a consumer.

When the temperature of gas that contain maximum of water vapor decreases, then condensation of the part of water vapor takes place. To reduce the temperature at which condensation of water vapor occurs, it is necessary to dry it. For industrial implementation, it is recommended to dry the gas with liquid absorbers, since its advantages are small investments and operating costs. The scheme of the process of gas drying with liquid absorbers is shown in Figure 2 (Ferencz, 2012; Churakaev, 1983; Kochi, 2013; Etvud, 2005).

At diethylenglycol dehydration (DEG), wet gas goes to the lower scrubbing part of the absorber (1) where it is freed from suspended hydrocarbon condensate and water. Then it passes through the central tube of the draw-off tray and contacts with DEG or TEG absorber water solution flowing from above. Gas, being on bubble trays, rises from tray to tray, the number of which depends on the design of the absorber and can be from 5 to 12; then gas is dried and goes to the upper scrubbing part of the column where the entrained drops of absorber are retained. Above the absorber, the dried gas goes to the destination. As the solution of the absorber flows down (from tray to tray), it is increasingly saturated with water, then it is gathered on a draw-off tray (stretching) of the absorber. The absorber operates under the same pressure, under which gas is sent to the dryer. To ensure the self-flow of the regenerated absorbent from the stripping tower or stripper (4) through heat exchangers (2) and the refrigerator (6) into the intermediate tank, the desorber is placed on a shell of 4-5 m high and the absorbent is sent from the tower to the next stage – regeneration. On exit from the absorber, the saturated absorbent successively passes the heat exchanger (2), the evaporator (3) in which absorbed gases are extracted from it, then it is passed by the second heat exchanger (2) and goes to the stripping tower at a temperature close to the boiling point (4).

Figure 2: The scheme of the process of gas drying with liquid absorbers (Ferencz 2012; Churakaev, 1983; Kochi, 2013; Etvud, 2005): 1 – Absorber; 2 – Heat exchangers; 3 – Evaporator; 4 – Stripping tower (strip column); 5 – Reboiler; 6 – Refrigerators; 7 – Intermediate tank; 8 – Pump. Flows: I – Raw gas; II – Dry gas; III – Weathering gas; IV – Water vapor; V – Regenerated absorbent; VI – Fresh absorbent; VII – Gas condensate



In the desorber, water vapor from the absorber solution is distilled. Gases and vapors of water released from the solution are emitted from the top of the tower into the atmosphere. Sometimes water vapor condenses and then is sent to the upper tray for a cold irrigation.

The stripping tower has 10-16 bubble-cap plates or valve type plates and one draw-off tray mounted 0.6-1.0 m below of the lower sieve tray. The absorbent gathered on the draw-off tray passes by gravity through a remote heater called a reboiler (5), and merges into the bottom of the column. In the heater, the absorber solution is heated by water vapor or another heat carrier. The absorbent inlet is at the bottom for better heat transfer, and the outlet is at the top. Thus, the heater is always filled with the absorber and the entire mass of the circulating absorbent passes through it bottom-upwards.

The regenerated absorber gathered in the lower part of the desorber (4) passes through the heat exchanger (2) where it gives off heat to the saturated absorber, then it passes through the cooler 6 to the intermediate tank 7 from which it is sent for irrigation. The desorber, as a rule, operates under atmospheric pressure or the pressure that is slightly higher (0.011-0.012 MPa). In some devices, the absorber is regenerated under vacuum.

The industrial practice of removing SO_2 and CO_2 impurities from APG involves the precipitation of acidic components with the help of solutions of mono-ethanolamines (MEA).

MEA absorbs H_2S and CO_2 along with the formation of sulfides, disulfides, carbonates and bicarbonates:

$$2RNH_2 + H_2S <=> (RNH_3)_2S, \tag{29}$$

$$(RNH_3)_2 + H_2S <=> 2RNH_3HS, \tag{30}$$

$$2RNH_2 + CO_2 + H_2O <=> (RNH_3)_2CO_3, \tag{31}$$

$$(RNH_3)_2\ CO_3 + CO_2 + H_2O <=> 2RNH_3HCO_3, \tag{32}$$

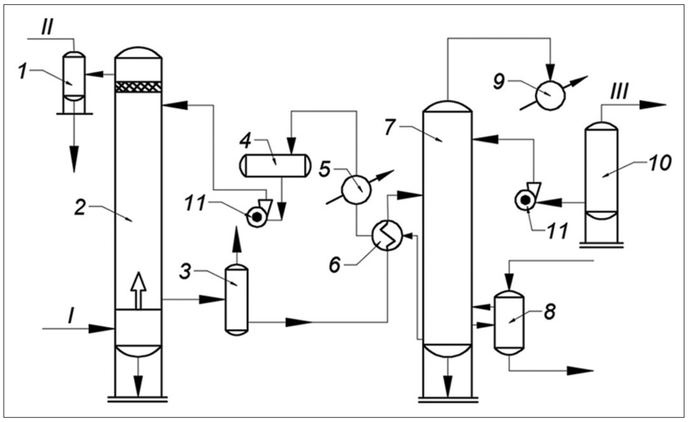
$$2RNH_2 + CO_2 <=> RNHCOONH_3R. \tag{33}$$

R is a residual in these equations CH_2-CH_2-OH.

The course of reactions is from left to right at the temperature of 20-40°C and the increased pressure; and the course of reactions is from right to left with the increase in temperature to 105-130°C and with the pressure close to the atmospheric one (Kirillov, 2014; Ferencz, 2012; Leontev, 2012; Pavlov et al., 1987).

Chemical reactions are carried simultaneously with the physical process of absorption. The driving force of absorption (diffusion) is the difference between the partial pressures of H_2S or CO_2 in the gas phase and MEA solution. H_2S and CO_2 molecules overcoming the resistance of the liquid film react chemically with MEA. The resulting products are removed very quickly from the interfacial area and they are distributed uniformly and fully in the solution. Therefore, the partial pressures of the absorbed acid gases in the solution do not increase but remain at the same level. Since the vapor pressure ratings of CO_2 and H_2S equilibrated with MEA are close to zero (or even zero), the absorption of acid gases with the solution is possible until MEA is chemically reactive with these gases. The basic scheme of the gas treatment unit for the solution of MEA is shown in Figure 3.

Figure 3: Gas treatment unit with the solution of mono-ethanolamine (Churakaev, 1983; Etvud, 2005): 1, 3, 10 – Separators; 2 – Absorber; 4 – Tank; 5, 9 – Refrigerators; 6 – Heat exchanger; 7 – Desorber; 8 – Reboiler; 11 – Pumps. Flows: I – Raw gas; II – Purified gas; III – Acid gases



In the gas treatment unit with MEA solution, the gas containing acidic components is sent to the lower absorber zone (2) in which it contacts the MEA solution. The process has counter-current flow; the gas flows bottom-upwards, the MEA solution is from the top downward. Absorption is carried out at pressures from 0.2 to 7.0 MPa. The absorber has 16-30 bubble plates.

The purified gas from the top of the absorber goes to the desorber 7 where it is released from the drops of the MEA solution. The solution saturated with sulfides, disulphides, carbonates and bicarbonates goes to the amine flash drum 3 from the bottom of the absorber. There hydrocarbon gases and some of the acid gases are released from the solution.

Individual point monitoring must meet the following criteria:

- To characterize for sure a pollution bubble (the pollution bubble is determined by the results of the dispersion calculations and subsequent analysis);
- To characterize the level of impact within the specific zone on people health and on the environment as a whole;
- To allow characterizing the contributions of the main sources of pollution.

The method of conducting observations (at a control point or by flare plume monitoring) is determined in each specific case and depends on the location of the emission sources and their type, as well as the composition of the pollutants emitted.

Table 10: Recommended schedule for compliance control with emission quota for an industrial facility using associated petroleum gas

Control point	Production, shop floor, shop area	Name of the harmful substance	Number of planned measurements in a period of time	Controlled parameters
On the boundary of SPZ	Oil-separator	Amount of hydrocarbons	Incomplete programme	Mass fraction of saturated hydrocarbons (in total), unsaturated hydrocarbons (in total) and aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylenes, styrene) with their joint presence in the atmospheric air, workplace air and industrial emissions
	Boiler (if any)	Sulphur dioxide	Once year	Mass fraction of sulfur dioxide in waste gases from boilers, thermal power plants, state district power stations and other fuelburn systems
	–	Carbon dioxide	Once year	Mass fraction of carbon dioxide from sources of burning of organic fuel
	–	Nitrogen oxides	Once year	Mass fraction of nitrogen oxides in operational emissions of boiler houses, thermal power plants and state district power plants
On the boundary of a settlement		Amount of hydrocarbons	Incomplete programme	Mass fraction of saturated hydrocarbons (in total), unsaturated hydrocarbons (in total) and aromatic hydrocarbons (benzene, toluene, ethylbenzene, xylenes, styrene) with their joint presence in the atmospheric air, workplace air and industrial emissions

SPZ: Sanitary protection zone

An observation program is developed for each point that includes a list of substances to be monitored, the composition of means and methods of measurement or calculation, frequency and time limits. To monitor the norms of maximum permissible discharges, the values of ground level concentration were determined at points on the boundary of the sanitary protection zone in the direction of the nearby residential development, and on the boundary of the settlement zone.

A potentially implemented schedule for compliance control with emission quota is presented in Table 10.

In concordance with the incomplete program, observations are made according to a staggered schedule: Tuesday, Thursday, Saturday – at 7:00, 10:00, 13:00, Monday, Wednesday, Friday – 15:00, 18:00, 21:00.

5. CONCLUSION

The incidence of losses of APG that is burned in flare devices is determined; as a result, a significant amount of pollutants (CO, CO_2, NO_x, and SO_2) are emitted into the atmospheric air. Based on the analysis of the existing practice, recommendations are formulated for the targeted use of APG with the change-over of boiler rooms designed for the use of natural gas produced as a result of processing of the APG. The implementation of such measures will make it possible to eliminate the irrevocable losses of natural energy carriers under the terms of self-repayment.

The paper can be summarized as follows:
1. Ecological and economic feasibility of using irreversibly lost associated gas of oil production is beyond doubt.
2. The processes associated with the operation of flare devices in oil production and refining facilities lead to irreversible environmental violations, primarily due to the burning of the atmosphere and its simultaneous large-scale pollution.
3. The implementation of integrated technologies for the use of associated gases should be a high-priority task for oil companies.

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