A NEW TECHNOLOGY TO PREVENT VOC EMISSIONS IN TANK BATTERIES

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ABSTRACT

VOC emissions control and development new methods for hydrocarbons losses prevention under tank storage is one of the important ways of the fuel and energy resources saving. A significant source of oil resources saving is VOC emissions losses prevention during their recovery, processing, transportation and storage in tank batteries. Control of hydrocarbons losses would result in saving about 20% of world hydrocarbon and energy resources and also prevent a negative ecological impact which grows out environmental pollution by oil products. Therefore losses control gives not only economic benefit, but also allows creating an environmentally friendly storage technology. Unfortunately, use of modern storage systems involves many constructive and technological difficulties such as floating roof jamming, losses of hydrocarbons within the tank walls, pollution of stored products by impurities from the atmospheric air, etc. The objective of this project was experimental study and mathematical simulation for developing new energy saving technology of hydrocarbons storage in tanks. Project was based on theoretical and laboratory researches on development of special device for storage tanks with adjustable gas equalizing system in order to prevent VOC emissions and atmosphere pollution. In this research project the basis of industry technology of hydrocarbons storage with adjustable gas gathering and equalizing system was developed. A systematic and fundamental study of rheophysical properties and hydrodynamic behavior of oil products was conducted in this project. Laboratory experiments were carried out to determine important evaporation properties of the test hydrocarbons using both the standard commercial and in-house made equipment. The obtained results will provide the valuable information for mathematical and Computational Fluid Dynamics (CFD) simulation of the hydrocarbon fluids flow in pipes and tanks under loading operations. As a result of the project we developed a special device - inflatable reservoir pontoon to prevent for hydrocarbon emissions in reservoir batteries of the oil recovery and refinery plants.

INTRODUCTION

Delivery of recovered hydrocarbons from oil fields to refinery, storage and consumption points entails extensive oil products losses. The losses occur all the way where hydrocarbons start moving from oil wells and until received by consumers. The losses related to the overflow, evaporation, weather factors, equipment imperfection, etc. are increased at the numerous transfers from one location to another. Transportation, storage and loading operations are always accompanied by product losses. The losses depending on fuel properties and external factors, such as air temperature, atmospheric pressure, etc. cannot be completely prevent, and they are considered as natural losses. The losses from evaporation are referred to such kind of hydrocarbons losses. There are also other types of losses such as product leaks and sprays. However, according to research data, approximately 75 % of losses of the liquid oil products are due to the evaporation.

A significant portion of the mineral oil evaporation losses are related to the high pressure saturated vapor under bulk storage and various operations connected with different loading operations. The hydrocarbon evaporation is concerned with not only material losses, but it also causes environment pollution by toxic hydrocarbons. Some hydrocarbons are capable to create photochemical reactions, causing atmosphere pollution by persistent combustion fog. Therefore, fuel losses reduction is an important economic and an environmental problem.

Annual Volatile Organic Compound (VOC) emissions under oil products storage, by various evaluations, are about 50-90 million tones[1]. A significant part of these emissions is from the oil refining plants and oil and gas production

[1] Кавнев Г.М., Моряков Н.С., Загвоздкин В.К., Ходякова В.А. *Охрана воздушного бассейна на предприятиях нефтепереработки и нефтехимии в связи с переходом на новые экономические методы управления*. М.: ЦНИИТЭнефтехим. 1989. (Тем. Обзор)

industries. Specific losses of hydrocarbons due to their evaporation at petroleum refineries are 1.1 - 1.5 kg per ton of the oil product. Only in Russia, annual hydrocarbon emissions to the atmosphere during oil production and refining are 1.168 thousand tons[2].

A significant atmosphere pollution by VOC emissions occurs during loading operations called "tanks breathing" in the oil storage. From the moment of oil recovery and before its use by customers, the oil products are exposed more than 20 transfers. 75% of these losses are due to the evaporations and only 25% are due to the failures and overflows. The large number of the "breathing" tanks is placed on the petrocrafts, oil-transfer stations and in tank batteries of oil refining factories. About 70% of all losses of mineral oil occur in tank batteries at the refining factories. Annual losses of mineral oil due to the "big breathing" on Russian oil refining factories are about 270 thousand tones (Figure 1).

An atmospheric pollution by VOC emissions occurs also during fueling railway tanks at platforms and motor vehicles at gas stations. Only in Russia[2] average total tank capacity of gasoline stations is around 240 million m^3. Approximately 130 million tons of various mineral oils are consumed every year. According to official data[3], annual atmospheric emissions from the gasoline stations in Russia are more than 140,000 tons of hydrocarbon VOCs, in Germany – 145,000 tones, in England – 120 tones. In USA there are about 573,000 crude oil storage tanks. These tanks are used for oil storage during the short period for flow stabilization between a productions well and the pipeline or loading point[4]. During the storage the light hydrocarbons dissolved in crude oil (including methane and other volatile organic compounds, gas condensate, dangerous air pollutions and other inert gases) are affected by various external factors (temperature fluctuations – "small breathings", repeated cycles of loadings operations – "big breathings", corrosion activity, etc.), increasing intensity of evaporation, and, hence, hydrocarbons losses, an atmosphere pollution and a fire risk.

Hydrocarbons losses under "big breathings" are caused by compression of a steam-air mix in the tank gas space under the action of loaded oil. Losses from the "big breathings" are defined by a number of factors: by volume, temperature and injected oil gas saturation, VOC concentration, pressure in gas space of storage tank, a kind of mineral oil and its breakup[5]. The vapour content in the gas space increases during tank loading, however the great bulk of hydrocarbon vapours is accumulated in the gas space during the oil storage[6]. The losses increase with the tank loading cycles and they also depend on the climatic zone. In average, annual losses from "big breathings" are about 0.14 % of the volume of stored mineral oil.

Reduction of hydrocarbons emissions can be achieved by various ways:

- improvement of hermetic sealing of storage tank
- reduction in absolute values of temperature in gas space and storage products
- reduction of amplitude of temperature fluctuations
- reduction of gas space volume in the tank
- catching hydrocarbons vapors formed in the tanks[7].

A schematic diagram of abovementioned methods is presented in Figure 2.
The major losses of mineral oil during its recovery, processing, transportation and storage are related to the evaporation in tanks and leakage. Losses due to the evaporation are a large portion of quantitative losses. However, due to the emission processes the light fraction of hydrocarbons evaporates and therefore qualitative changes of mineral oil structure take place. In any cases the significant losses of light fractions of gasoline the oil product was unsuitable for the customer requirements.

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[2] Федеральный справочник "Топливно-энергетический комплекс России". "Родина-Про", 1999.

[3] Транспорт и хранение нефтепродуктов // Научно-технический информациионный сборник. М.: 1997. № 1.

[4] *Evaporative Loss From External Floating Roof Tanks*, Third Edition, Bulletin No. 2517, American Petroleum Institute, Washington, DC, 1989.

[5] David C. Trumbore Estimates of Air Emissions from Asphalt Storage Tanks and Truck Loading Asphalt Technology Laboratory. - Environmental Progress, Vol.18, No.4. – pp.250-259.

[6] Ferry, R.L., Estimating Storage Tank Emissions--Changes Are Coming, TGB Partnership, 1994.

[7] Laverman, R.J., *Emission Reduction Options For Floating Roof Tanks*, Chicago Bridge and Iron Technical Services Company, Presented at the Second International Symposium on Aboveground Storage Tanks, Houston, TX, January 1992.

Losses at “small breathings” are caused by fluctuations of the ambient temperature. During the sunny days the tank surface will be heated up, and it will result in an increase of the mineral oil evaporation, and especially light fractions. Hence, pressure and temperature of gas-vapor mixture inside the tank will be increased. Pressure growth entails an operation of the respiratory valve and atmospheric emissions of VOC accumulation. During the nights when the stored products are cooled down the pressure of the mixture will be reduced. Hence, the vacuum will be created and a return phenomenon may be observed, e.g. the air through the inlet valve penetrates into the gas space of the tank. The problem of hydrocarbons losses prevention in storage tanks has been investigated by Yufin V. A. and Anohin A. V.[8], Popovski B. V.[9], Abuzova F. F., Bronshtein I. S. and Novoselov V. F. [10]
The methods of reduction of losses in the storages of mineral oils are the followings:

1) **Reduction of the gas space volume**. It is reached in tanks with floating roofs and pontoons. The pontoon is a hollow disk. The evaporation losses can be reduced up to 90 %. In tanks with a floating roof a gas space is almost eliminated, and the losses from the big and small breathings are prevented.
2) **Storage hydrocarbons under high pressure** in special designed tanks.
3) **Reduction of temperature fluctuations in the gas space** of the tank (thermal insulation, water cooling in summer time and underground storage).
4) **Recovery of vapors in the tank**. The wide distribution the network system of gas pipelines, connecting through the gas equalizing lines, which connect tanks’ gas spaces among themselves.
Various methods and devices are used to VOC recycling (reduction of losses) during the storage of oil:

- gas equalizing systems;
- torch burning;
- membrane separation of VOC;
- nitric cooling;
- adsorption (using an activated coal);
- absorption (using oils);
- floating roofs;
- pontoons, etc.
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All these technologies have both advantages and disadvantages. The general drawback is that they cannot be well-provided for VOC recovery. One of the VOC emissions reduction techniques is application of recovery setups for hydrocarbons light fractions. Now there are some types of such installations with various design and principles of work. A wide application of such installations was found in tank batteries of "Tatneft" Oil Company (Russia). High efficiency of this type of installations are combined with a number of lacks: they are expensive, have a heavy equipment and a control system, need dry gas consumers, etc. The Russian researchers developed a technology of VOC recovery on the basis of *Sterling* low-temperature refrigerators (sterling-technology). This technology considers a class of condensation systems. VOC recovery occurs due to their cooling to the subsequent condensation. *Sterling* low-temperature refrigerators work at temperature as low as -250°C. A wide spectrum of light hydrocarbons will liquefy at atmospheric pressure. *Sterling* low-temperature refrigerators for cooling and condensation of gaseous hydrocarbons are applied on mobile gas trucks. Multi-purpose gas trucks such as «Pythagoras», «Teviot», «Lincoln Ellsworth» and «Thales» are intended for transportation of methane, ethane, propylene, prosier, butane, etc. During the transportation the temperatures varies from -160°C to -10°C.
Last few years some of the companies engaged in storage and processing of hydrocarbons preferred tanks with pontoons. Such tanks, having all advantages of tanks with floating roofs, at the same time they eliminate necessity of the devices and services of drainage systems, contamination and hazards. They improve operating conditions of condensing shutters. One more advantage of such tanks is their working capacity in a wide temperature ranges. A number of tanks with pontoons for crude oil storage were constructed last years in the North America. In a tank farm of «Texaco Paragon» in Newark there is a tank with a pontoon of 40,000 $м^3$ volume. Similar tanks were designed also by Pittsburg D’Moin Steel Co. and Chicago Bridge and Iron Co.

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[8] Строительство и эксплуатация резервуаров нефти и нефтепродуктов», Москва, ЦНИИТЭнефтехим, 1968

[9] Уплотнения для резервуаров с плавающей крышкой и понтоном, НТС, «Транспорт и хранение нефти и нефтепродуктов», №2, Москва, ВНИИОЭНГ, 1969

[10] Борьба с потерями нефти и нефтепродуктов при их транспортировке и хранении, Москва, Недра, 1981

In France tanks with pontoons are built by «Larouch Buvier». Such tanks are constructed in Strasbourg and Paris. A "PDM Interfloat" type pontoons are constructed by Pittsburg D'Moin Steel Co.

The recent advances in development and manufacturing of synthetic elastic and rubber fabric materials with oil-resistant properties allowed developing nonmetallic pontoons. For example, *Тоё Канецу Koto K.K.* developed pontoons from rubber-fabric membranes.

In England Nayler Petrosil Ltd has developed and widely utilized the pontoons of «Niflex-Jirco» type consisting from periphery-type ring from curved fiberglass segments and internal flooring from steel rectangular sheets. The flooring is laid on supporting floating construction which is made of blocks of the rigid polyfoam covered by fiber glass.

The «Union Carbide and Carbon Corporation» has developed and tested a technique of mineral oil losses reduction in tanks by means of a covering of a fluid surface by layer of micro balls. These balls are microscopic hollow bubbles from the phenolic pitch filled by nitrogen. A drawback of this technique is that micro balls are subjected to harmful action of water. It causes leaching process that leads eventually to the destruction of the smallest balls.
A wide utilization of many new techniques is limited due to the number of the essential constructive and technological problems complicating their application, such as:

- sinking and jamming of floating covers and pontoons because of non-uniform load due to the atmospheric precipitations and formation of firm adjournment on tank walls;
- hydrocarbons losses from tanks walls;
- pollution of storage production by impurities in atmospheric air;
- increased fire risk.

The disadvantage of currently used mineral oil storage tanks, in particularly a method of storage under high pressure, is that under the certain pressures (1,000-2,000 Pa) the hydrocarbon gases are dumped into the atmosphere. These gases may also escape into the atmosphere through macro- and micro-cracks formed in the roof and joints during and between the repair periods. Because of the duration between the repairs (2 years and more), locations of the leaks of hydrocarbon gases will be detected with delay. It will result in a pollution of atmospheric air around tank batteries and the environment. For example, ulcer and pitting corrosion (0.2-0.9 mm/years) result in the formation of randomly located apertures of 5-6 mm in diameter during the time period from 4 months to 4 years.

A severe destruction of tank roofs occurs during the storage of oils containing sulphuric acid, and a in the tank batteries with long term operation. The hydrocarbon vapors' leak into the atmosphere through apertures and cracks leads to the failure of the gas exhaust system. Hence, the hydrocarbons will be released to the atmosphere, polluting air in a working zone and in adjoining territory with excess of maximum-permissible concentration (12 %).
Various storage techniques using hollow pontoons cannot prevent VOC emissions during the fluctuations of the liquid level in storage tanks. Also the pontoon is not tightly touches the liquid free surface and therefore, the vapors of VOC above pontoons will appear.

Therefore, the new technologies of VOC emissions reduction during the storage in tank batteries are needed to be developed.

PROJECT OBJECTIVES

The objective of the project was the development of energy and resource saving technology of hydrocarbons storage based on theoretical, laboratory and industrial researches to develop inflatable tank pontoons in order to prevent VOC evaporation and environmental pollution. It was proposed to tank pontoons from oil-resistant rubber-textile or synthetic material, closely fitting an internal surface of the tank in order to maintain a constant pressure during loading and emptying operations (Figure 3). Such pontoons are equipped with means for their fastening to the top of the tank. Maintenance and dump of pressure in a pontoon space is carried out by means of the compressor and gas collectors connected to the pontoon via an automatic pressure regulator.

The essential feature of the process must be a maintaining of the constant pressure in pontoon space during the tank loading and emptying processes. To ensure that the pontoon volume is equal to the volume of empty space above the surface of stored product, a pontoon's inner space is connected to the compressor and gas collector via automatic pressure regulators. Thus, when the liquid level in the tank is reduced gas will be pumped into a pontoon using a compressor, and when the liquid level is increased part of gas is released from a pontoon by special pressure device. Proposed process provides reliable hermetic sealing of space between the surface of stored product and a tank roof. Thus, a formation of a free volume in the tank space will be avoided (Figure 3).

In case of tank battery the pontoon spaces can be connected among themselves by means of a gas line (Figure 4). The technology provides installation of compressor gas line and gas collector with automatic pressure regulators. During simultaneous loading of some tanks and emptying other tanks of the battery, gas will flow from filled tanks to the emptied ones, and its surplus or lack can be compensated by pumping of gas or its emissions into the gas collector. When the part of tanks are only filled (or emptied) the gas exchange will be realized only between the compressor (or gas collector) and pontoons.
The project consisted of theoretical studies of effects of various factors, such as an evaporation surface area, vapor pressure in tank gas space, temperature fluctuations, and also periodic fluctuations of the surface of stored product on VOC evaporation intensity. A mathematical model of evaporation process with various volume and componential structure of gas space was developed.

The effect of periodic fluctuations on a free surface of stored liquids is high in case of use of mobile fuel tanks, and also by transportation liquid hydrocarbons by tankers and gasoline tank trucks.
The results of preliminary studies of the effects of free fluctuations of viscous liquid with free surface have shown that a speed of fluctuations attenuation is significantly lower than calculated values with consideration the liquid viscosity. The given effect is necessary for considering under calculation of hydrocarbons losses under their storage and transport, since those fluctuations of liquid free surface have impact on evaporation speed. In the project development of mathematical model of periodic fluctuations an impact on evaporation intensity was taken into the consideration.

The offered technology has enough high innovative potential connected not only with improvement of ecological situation, but also significant volumes of saved products.
Use of results of design researches can be carried out at the oil recovered enterprises, petrochemical, a petroleum-refining industry, at oil loading stations with storage of wide range of production volumes.

RESULTS

A new technology and the device on the basis of inflatable tank pontoon were developed. A concept of the special gas equalizing system (GES) was developed to reduce or prevent VOC emission of stored oil products.
International patent on new technology for preventing VOC emission is applied.
Results of experimental and theoretical researches are supposed to apply on the oil and gas recovery and oil refining enterprises, in particular oil and gas extraction enterprises.
Application of evaporation prevention technology by inflatable pontoons and gas equalizing systems will allow:

- to keep that part of mineral oil which earlier was lost irrevocably in connection with absence of modern effective methods of VOC recycling;
- to receive additional profit on selling of saved production;
- to improve environmental and working conditions of the personnel not only at tank farms, but also in the surrounding areas;
- to reduce fire risk of petroleum storage depot, to increase service life of tanks, etc.

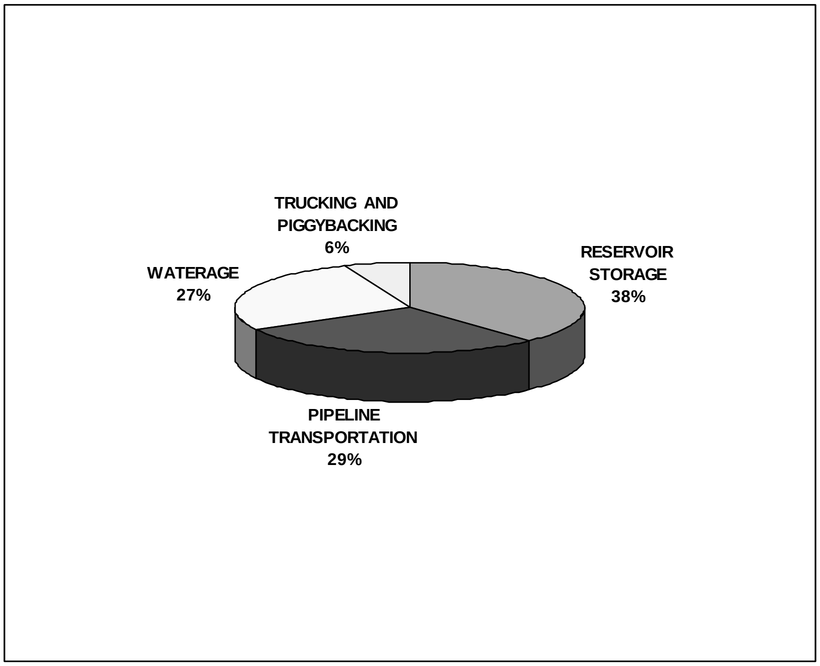

Figure 1 - VOC Losses in Various Oilfield Operations

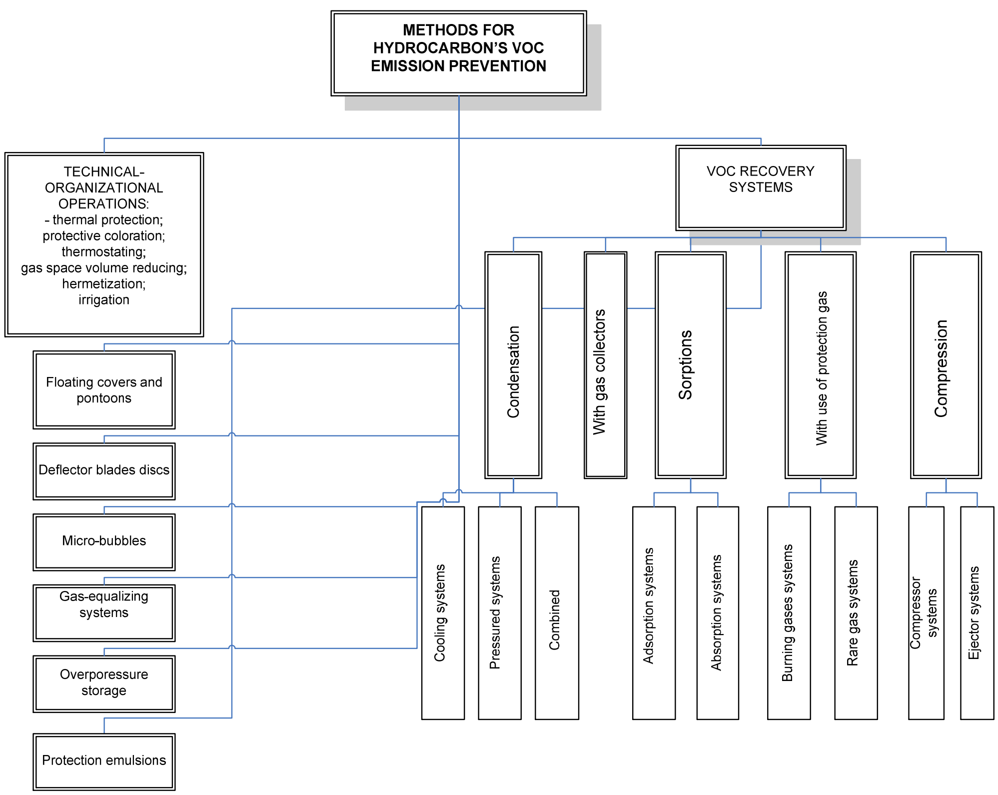

Figure 2 - Methods of VOC Emission Prevention

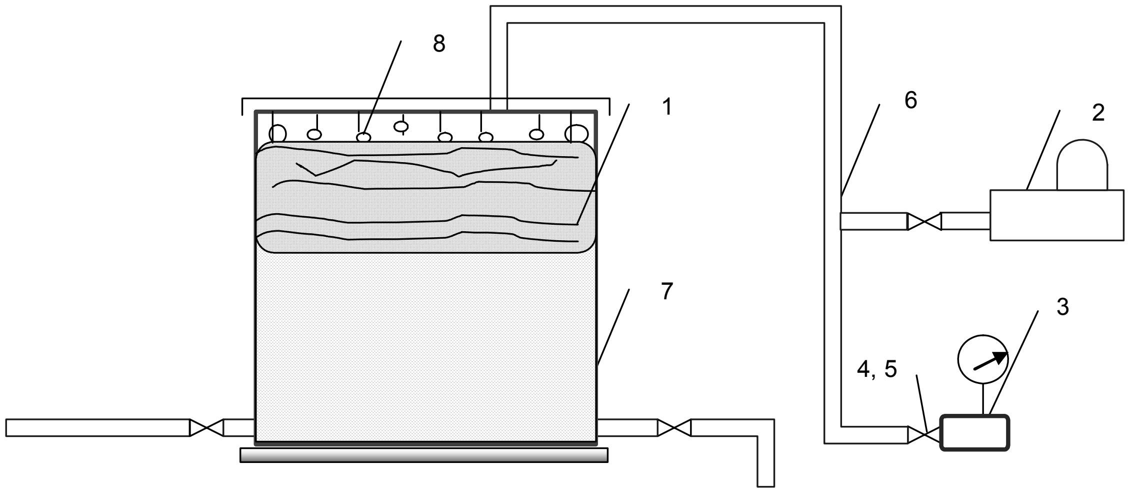

Figure 3 - Schematic of new technique: 1- inflatable pontoon; 2 - compressor; 3 – gas collector for pressure release; 4, 5 – automatic pressure regulators; 6 – gas lines; 7 - tank; 8 – pontoons fastening accessories.

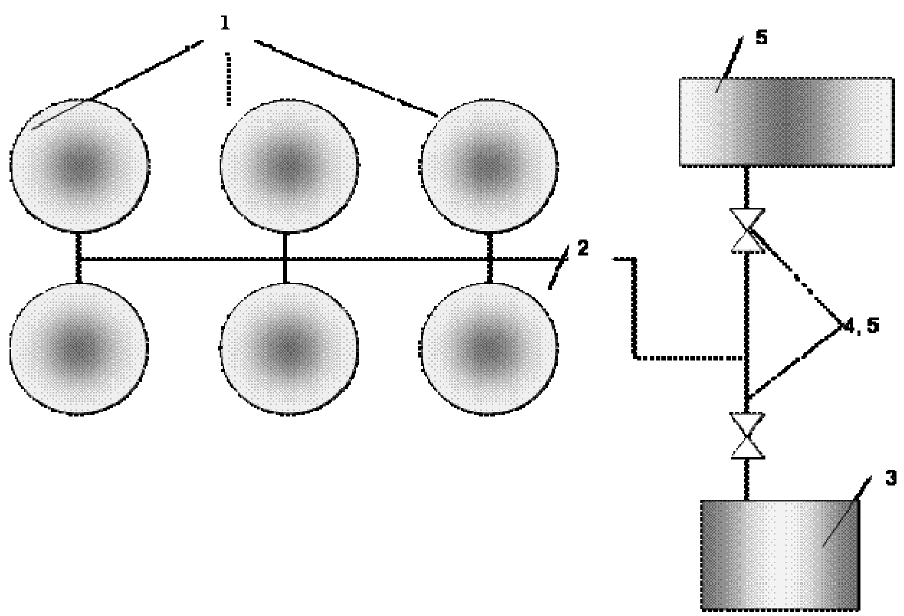

Figure 4 - Tank batteries: 1 – tanks; 2 - gas lines; 3 – compressor; 4, 5 – automatic pressure regulator; 5 – gas collector.