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Development of a New Method for Reducing the Loss of Light Hydrocarbons at Breather Valve of Oil Tanks

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Abstract

This work including, the possibility of reducing the loss of light hydrocarbons by introducing micro-quantities of an additive having surface-active properties as new method. There have been successful attempt to use free fatty acid (FFA) on the form of artificial salt to reduce the loss of light hydrocarbons. The optimal concentration of this salt was determined by estimating the lowest pressure saturated with steam its (8 mg/kg). It was found that the evaporation rate reduced to 47% in the oil tanks. It has been observed that the effect of adding this compound to the oil tank is to be slightly, it was also found that the presence of artificial salt compound at the bottom of the tank is 10%. In this case, it appeared to be advantageous to use this method for reduce the loss of light hydrocarbons, which should prevent the loss of light hydrocarbons.

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1. Introduction

The problem of reducing losses of light hydrocarbons of petrol all the way from storage to the application is very urgent. The solution of this problem is not only environmental, but it is also economic (loss of oil because of evaporation in Russia only may be 500 - 600 thousand tons per year), but this is less than in countries near the equator, due to high temperatures in comparison with Russia. Air in the summer warms up in Iraq, for example, to (35 - 47 °C) in winter to (10-20 °C) [1-10].

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Upon delivery of oil from refineries to consumption, there are significant losses. According to studies, more than 75% loss of oil due to its evaporation is detected. Evaporation losses occur during storage, draining, filling, transport, refueling and application (from the fuel tanks of vehicles, from the carburetor bowl, etc.). In addition to material losses, evaporation of oil is often accompanied by a deterioration of certain performance level that contaminates the environment. Therefore, a well-organized, coherent and systematic struggle with losses from evaporation of oil at all stages of transportation and storage is of great importance in the whole country [5,11, 12].

When operating technically serviceable handling of oil products and vehicles, the main losses of oil from evaporating occur in the tanks. The loss of oil in the tanks results in the spread of the gas in the atmosphere or the space. Under ordinary conditions of storage of petrol in the tank, gas space is filled with a mixture of air and oil vapors. With increasing ambient temperature (e.g., in the afternoon on a sunny day), oil is heated and steam mixture expands (the pressure is on the increase). To prevent the destruction of the reservoir, a valve at which some of the work-steam mixture to the atmosphere (so-called small breathing) is placed at the top of the tanks. In the evening, during cooling of the tank in the gas space of a vacuum the air enters into the reservoir through a valve [2,6,7-14].

The composition of hydrocarbons in urban air is closer to the composition of oil than the composition of exhaust gases from automobiles. This shows that one of the major sources of emissions of hydrocarbons into the air in our cities are a loss fuel evaporation from the fuel systems of engines and the refueling of cars at gas stations [1,2,11,12].

According to the European Commission on the Environment, with each operation plum (loading) of oil in the atmosphere 0.5-1.5 kg hydrocarbon vapor for each cubic meter of transfused fuel [1,15-17].

Currently, in accordance with the recommendations of the European Commission on the Environment, which are mandatory for all EU countries. The commission has introduced regulations on vapor recovery of hydrocarbons throughout the supply chain handling, storage and distribution of light hydrocarbons, and by 2000 all petrol stations, and by 2002 -2004 years. All oil storage tank farms, ramps and terminals loading of light oil products (including trucks) should be equipped with oil vapor recovery systems , providing complete capture at least 80% [18-21].

The solution of the environmental problem requires large capital investments in the coming years, yet it is not feasible in Iraq. After the transition to unleaded oil, refiners increased use of butane as a high-octane oil component, resulting in a significant increase in vapor pressure of oil, which in turn led to increased losses of hydrocarbons and consequently, to increase the level of air pollution, especially in summer. The problem of air pollution led to the emergence of new regulations limiting the vapor pressure, thus reducing the possibility of using low-cost, high-octane, environmentally friendly oil component - butane [11,22].

Investigation ways that can reduce the loss of oil from evaporation during storage, transport, loading and from the engine fuel system, do not require the cost of reconstruction of existing equipment for storing, transporting and unloading operations [12,23-26].

The objective of this paper is to a concise look at the method for estimating the loss of oil from the tanks, and improves the environmental safety of petrol stations based on developing a method to reduce the vapor pressure of oil.

2. Materials and Methods

2.1 Characterization

Determination of saturated vapor pressure according to the Reid vapor pressure (RVP) was performed in accordance with GOST standard 1756-2000. The design of the instrument for the studies is shown in Figures 1 and 2. For samples with a vapor pressure below 180 kPa, a liquid chamber with a single hole was used (figures 1 and 2).

2.2 Materials

It consists of elements of a surfactant into oil octave material which reduces the concentration of hydrocarbons at the boundary of oil - air, thereby reducing the vapor pressure and thus reduce the loss of oil from evaporating. As the used components were salts containing different metals Free fatty acid artificial (FFA) ($C_nH_{2n+1}COOH$), when $n = 10 -15$. Materials were selected for study, FFA (Free fatty acids artificial), Sodium hydroxide, Distilled water, Oil.

The basis is taken of oil (from the Shaim deposit). The oil in this field is low-sulfur 0.46%, resinous (10.19%, silica gel, 0.82% asphaltene, 2.08% as coking) and 2.89% waxy. The content of light distillates boiling up to 350 °C is 58.8%, that is, as we see, the yield of light fractions is quite high.



Figure 1. Vapor pressure measurement instrument

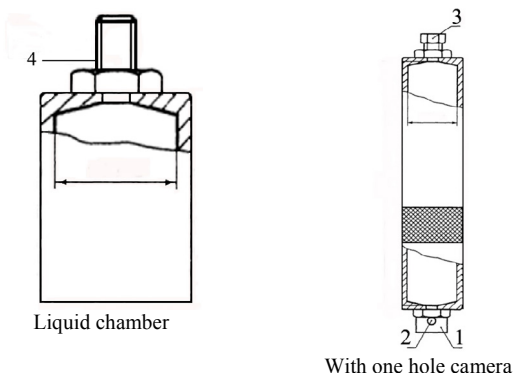


Figure 2. Bomb for determination of vapor pressure
(1) Connecting internal (2) Air vent (3) Connecting inner (4) External connection

In the study, it was taken into account that vapor losses are usually associated with light hydrocarbons (from C1-C5). The main characteristics of the Shaim oil are shown in Tables 1 and 2.

Table 1. Physical and chemical properties of the Shaim oil

| | |
|---|--------|
| Density ρ_4^{20} | 0,8269 |
| Molecular mass | 202 |
| Viscosity kinematic V_{20} , cCT | 6.80 |
| Viscosity kinematic V_{50} , cCT | 2.98 |
| The pour point with processing, °C | -2 |
| The pour point without processing, °C | - |
| The flash point in a closed crucible, °C | -35 |
| Saturated vapor pressure at 38 C ⁰ , mm.Gt; Art. | 322 |
| Paraffin content,% | 2.89 |
| The melting point of paraffins, °C | 55 |
| Sulfur content,% | 0.49 |
| Nitrogen content,% | 0.10 |
| Resin content of acidic,% | 14 |
| Resin content of silica gel,% | 10.19 |
| Asphaltenes content,% | 0.82 |
| Coking ability,% | 2.08 |
| The content of naphthenic acids,% | 0.043 |
| Fraction output up to 200 °C | 32 |
| Fraction output up to 300 °C | 58.8 |

Table 2. Composition of gases (before C₄) dissolved in oil and low-boiling hydrocarbons (C₅)

| Content of individual hydrocarbons,% | Fraction | |
|--------------------------------------|----------------|----------------|
| | C ₄ | C ₅ |
| C ₂ H ₆ | 1.20 | 0.70 |
| C ₃ H ₆ | 25.80 | 15.40 |
| I- C ₄ H ₁₀ | 17.20 | 10.20 |
| n- C ₄ H ₁₀ | 55.80 | 33.20 |
| I- C ₅ H ₁₂ | - | 13.40 |
| n- C ₅ H ₁₂ | - | 27.10 |
| Exit (For oil),% | 3.50 | 5.88 |

2.3 Methods of conducting laboratory studies

2.3.2 Method of preparation of the composition

A solution consisting of elements, NaOH and distilled water, with an equal number of moles, was prepared. Gradually, 10 gm of FFA were added at temperature of 600 °C. The solution was constantly mixed until the reaction was completed. The resulting solution was cooled to room temperature and left for 3 days, in order to evaporate excess water.

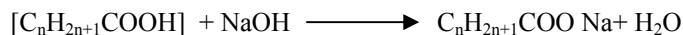
2.3.2 Investigation of the influence of surfactants on the reduction of light hydrocarbons losses on oil

The study was carried out by introducing into the oil a surfactant that reduces the concentration of hydrocarbons at the oil-air interface, which reduces the elasticity of saturated vapors and thereby reduces the loss from evaporation. As components, FFA salts containing different metals were used: FFA (C_nH_{2n+1}COOH), where n = 9-15.

A preliminary assessment of the effect of surfactants on reducing the loss of light hydrocarbons was made on the basis of a series of experiments on oil. To prepare a Na -surfactant solution, 10 gm of distilled water and 2 gm of potassium hydroxide were first mixed, then added to 10 g of FFA at 60 °C with constant stirring until the reaction is complete.

3. Results and discussion

The results of studies of the effect of surfactants (C_nH_{2n+1}COONa) on the saturated vapor pressure of a model fluid. In the course of the experiment additives were added to gasoline in various concentrations (1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12, 13 mg / kg). As a result of the experiment it was revealed that the minimum pressure is reached at a concentration of C_nH_{2n+1}COONa of 8 mg / kg. With an increase in the surfactant concentration, the saturated vapor pressure rises (Table 3, Figure 3).



When n= 10-15

Change the saturated vapor pressure of oil, depending on the concentration of C_nH_{2n+1} COONa given in table and figure 3.

Table 3. Vapor pressure of the model medium.

| Concentration $C_nH_{2n+1}COO Na$ mg/Kg | Saturated vapor pressure of oil, kPa |
|---|--------------------------------------|
| 0 | 60.5 |
| 1 | 58.9 |
| 2 | 50.7 |
| 3 | 44.4 |
| 4 | 40.6 |
| 5 | 41.5 |
| 6 | 37.8 |
| 7 | 34.2 |
| 8 | 32.1 |
| 9 | 35.8 |
| 10 | 39.7 |
| 11 | 41.0 |
| 12 | 46.6 |
| 13 | 50.9 |
| 14 | 60.5 |

The dependence of the saturated vapor pressure of oil, kPa from concentrations $C_nH_{2n+1}COONa$

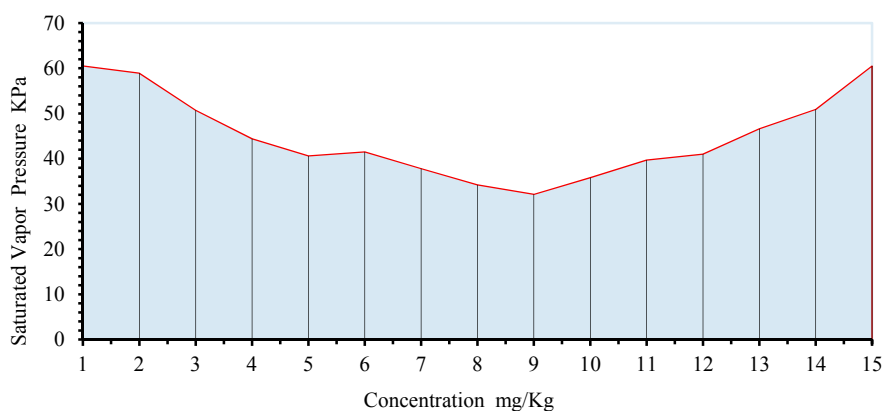


Figure 3. The dependence of the saturated vapor pressure of the model medium on the concentration of $C_nH_{2n+1}COONa$

Table 1 and Figure 1 show that introduction of $C_nH_{2n+1}COONa$ micro quantities to reduce the vapor pressure of oil. Concentration of 8 mg / kg is the most optimal, because of so much saturated vapor pressure minimum.

The minimum saturated vapor pressure was observed at a concentration of potassium salts of FFA 8 mg / kg, with further increase in the surfactant concentration, the saturated vapor pressure will increase. The observed phenomenon is explained by the fact that the surfactant occupies part of the evaporation surface without interfering with condensation, and when the surfactant concentration increases above the optimal value, an association of surfactant molecules occurs, which leads to an increase in the evaporation surface [3].

Next, a series of experiments were performed with the introduction of a 8% w / w oil into the first portion of the oil and a substitution in the subsequent experiments of the lower layer of the model medium (90% of the total layer) for oil without surfactants.

Table 4 and Figure 4 show the results of the influence of surfactants on the pressure of saturated oil vapors. Experiments were carried out successive replacements of the lower (90% overall) of the layer that contains no additives of oil in the first experiment in the petrol was introduced 8 mg / kg $C_nH_{2n+1}COONa$ for 1 kg of oil.

Change the saturated vapor pressure of oil at the sequence puff experiments are shown in the table 4 and in figure 4.

Table 4. Saturated vapor pressure of the model medium, depending on the number of experiments, with the addition in the first experiment of 8 mg / kg of oil e additive

| Number of experiments | saturated vapor pressure, kPa | Number of experiments | saturated vapor pressure, kPa | Number of experiments | saturated vapor pressure, kPa | Number of experiments | saturated vapor pressure, kPa |
|-----------------------|-------------------------------|-----------------------|-------------------------------|-----------------------|-------------------------------|-----------------------|-------------------------------|
| 0 | 60.5 | 15 | 40.7 | 30 | 53.8 | 45 | 58.8 |
| 1 | 32.1 | 16 | 41.0 | 31 | 54.2 | 46 | 58.9 |
| 2 | 32.1 | 17 | 42.2 | 32 | 55.0 | 47 | 59.3 |
| 3 | 32.6 | 18 | 42.4 | 33 | 55.1 | 48 | 59.4 |
| 4 | 32.7 | 19 | 42.5 | 34 | 55.9 | 49 | 59.5 |
| 5 | 33.0 | 20 | 42.6 | 35 | 56.5 | 50 | 59.5 |
| 6 | 33.4 | 21 | 42.8 | 36 | 56.7 | 51 | 59.5 |
| 7 | 33.5 | 22 | 50.1 | 37 | 56.9 | 52 | 59.7 |
| 8 | 34.3 | 23 | 50.6 | 38 | 57.4 | 53 | 59.8 |
| 9 | 34.4 | 24 | 51.0 | 39 | 57.5 | 54 | 59.9 |
| 10 | 35.0 | 25 | 51.7 | 40 | 57.5 | 55 | 59.9 |
| 11 | 36.2 | 26 | 51.9 | 41 | 57.8 | 56 | 59.9 |
| 12 | 36.8 | 27 | 52.3 | 42 | 58.3 | 57 | 60.5 |
| 13 | 36.9 | 28 | 53.4 | 43 | 58.4 | | |
| 14 | 40.2 | 29 | 53.4 | 44 | 58.4 | | |

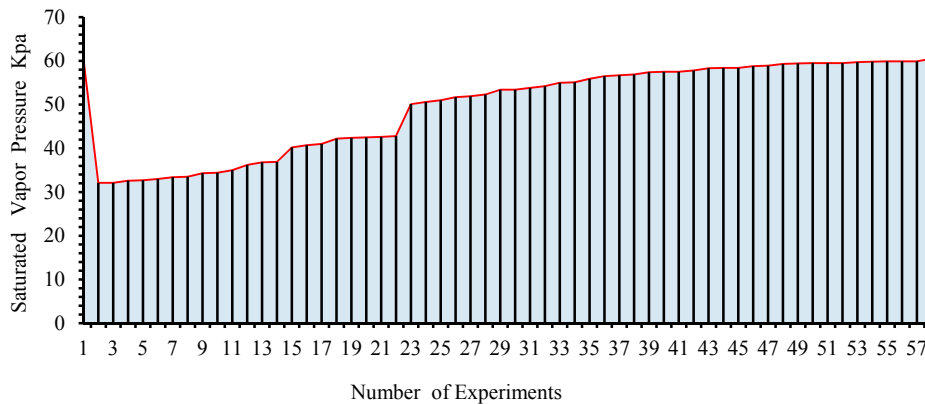


Figure 4. The dependence of the saturated vapor pressure of oil on the number of experiments

Assigned data show that a single injection of surface -active additive reduces the vapor pressure of approximately 57 Replace the lower layer (90% of the total) because of the concentration of additives in the upper layer. Fatty acid salt $C_nH_{2n+1}COONa$ was used to reduce the saturated vapor pressure in oil tanks, because all known surfactant methods have been used only for gasoline tanks, it has been pointed that the compounds are non-toxic and are not harmful to the health of workers, because in toilet soap contains more of these compounds. Confirmation on GOST standard 12.1.007-76). This surfactant compound do not influence the process of oil refining, because:

- they are obtained from FFA, and FFA is obtained in the process of distillation of oil.
- they are added to the oil in scant amounts.

Fatty acid salts are cheaper than others, because one ton of FFA costs 300 \$. In the Russian Federation, when oil is extracted at about 650 million tons a year, the loss of light hydrocarbons from oil is at least 3.2 million tons per year, while in the Republic of Iraq, with the extraction of oil of about 200 million tons per year, the loss of light hydrocarbons from oil is 1 million tons per year as a minimum, which is definitely unacceptable.

The possibility of reducing the losses of light hydrocarbons during the evaporation of oil without the equipment of oil reservoirs is 47%. So, if it will use this surfactant (Na FFA salt), the total cost is 1950 \$, per year when applied during the year 6.5 tons from $C_nH_{2n+1}Na$.

4. Conclusions

With respect to reduce the loss of light hydrocarbons, it is possible to use a concentration of (8 mg / kg) from the free fatty acid (FFA) on the form of artificial salt ($C_nH_{2n+1}Na$), thus preventing the evaporation of light hydrocarbons from oil tanks, and from fuel depots or modes of transport, also recommend using this method by all countries, which is located near the equator and remote, in order to preserve the wealth of oil, as well as conservation of the environment and the formation of a pollution-free environment.

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