Estimation of the Heat Balance of the Liquid Hydrocarbons Evaporation Process from the Open Surface During Geotechnical Monitoring

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Abstract. Researchers in Tyumen State Oil and Gas University (TSOGU) have conducted a complex research of the heat and mass transfer processes and thermophysical properties of hydrocarbons, taking into account their impact on the reliability and safety of the hydrocarbon transport and storage processes. It has been shown that the thermodynamic conditions on the surface and the color of oil influence the degree of temperature rise in the upper layers of oil when exposed to direct solar radiation. In order to establish the nature of solar radiation impact on the surface temperature the experimental studies were conducted in TSOGU on the hydrocarbon evaporation and the temperature change of various petroleum and petroleum products on the free surface with varying degrees of thermal insulation of the side walls and bottom of the vessel.

1. Introduction
The consequences of accidents and incidents on oil pipelines continue to exacerbate environmental problems. When analyzing accidents or forecasting risks, it is advisable to use a systematic approach (figure 1) treating each of them as a complex system, where many of the factors included in it (the duration of repair and recovery period, natural and meteorological conditions, the nature of the damage, pumping mode, emissions and others) are interdependent due to the rapid dissipation of mass exchange transitions and anthropogenic processes.

The scope of expert calculations of leaks and hydrocarbon emissions during their pipeline transportation is very extensive. From the typical problems that can be solved by experts at various levels, it is necessary to note the following:
• evaluation and prediction of reliability and safety indicators;
• assessment of the degree of emission hazard, taking into account its volume, toxicity, physical and chemical properties;
• prediction of accident consequences;
• compilation of a list of possible events during the propagation of leakage and emission;
• determination of the most likely time intervals between failures;
• determination of the examination results reliability and creation of a databank;
• assessment of the possible terms of the accident elimination;
• calculation of financial, material and labor resources and their minimization, etc..

Forecasting the effects of accidents should be based on reliability indicators, maintainability in particular, since the period of spill elimination is both a probabilistic and deterministic function.
A method for planning works and forecasting consequences of an accident should take into consideration (figure 2) the evaluation of the feasibility of the accident response plan for a variety of reasons.

For instance, the maintainability indicator for the main pipeline facilities - the average time of unscheduled (emergency) recovery (repair) $T_{rep}$, according to statistics, according to current regulatory documents, is estimated by (1):

$$
\overline{T_{rep}} = \frac{1}{r} \sum_{i=1}^{r} T_{rep}^i,
$$

Figure 1. Functional structure of a multilevel modular geotechnical monitoring system for a PS (pipeline system).

Figure 2. Stages of forecasting the consequences of accidents during an oil spill.
r - the number of failures that occurred during the observation period t; 
t_{wi} - the recovery duration time after the i\text{th} failure

Standard recovery time \( T_{i,\text{rep}}^{\text{reg}} \) for each i\text{th} accident should be estimated according to the formula in case of routine situations

\[
T_{\text{reg}}^{\text{rep}} = \sum_{i=1}^{n} T_{i,\text{rep}}^{\text{reg}} P_{\text{reg}}^{i}
\]  

(2)

The authors propose to assess the forecasted recovery time \( T_{i,\text{pred}}^{\text{rep}} \) in total and for each i\text{th} accident \( T_{i,\text{pred}}^{\text{rep}} \) from the condition (figure 3):

\[
T_{\text{pred}}^{\text{rep}} = \sum_{i=1}^{n} T_{i,\text{pred}}^{\text{rep}} P_{\text{pred}}^{i} + \sum_{i=1}^{n} T_{i,\text{pred}}^{\text{rep}} P_{\text{prod}}^{i}
\]  

(3)

where \( P_{\text{pred}}^{i} \) - the likelihood of i\text{th}-type emergency situation occurrence during repair.

\[P_{\text{reg}} = 1 - P_{\text{reg}} \]

Figure 3. State chart diagram for system recovery considering the time spent.

In its turn, the likelihood \( P_{\text{prod}} \) will be determined by:

\[
P_{\text{prod}} = P_{\text{pred}}^{1} + \ldots + P_{\text{pred}}^{n}
\]  

(4)

\( P_{\text{prod}} \) - the likelihood of standard condition occurrence for repair and recovery works. \( P_{\text{reg}} \) can be estimated statistically; however, conditions of emergency response may differ significantly from each other, which makes the error of calculations unreasonably high.

To estimate the probability of emergency situations it is advisable to establish a multi-factor model to estimate \( P_{\text{reg}} \) using deterministic components:

\[
P_{\text{reg}} = f(x_{1}, x_{2} \ldots x_{n})
\]  

(5)

where \( x_{1}, x_{2} \ldots x_{n} \) - factors that determine the possibility of carrying out the recovery work (technological, meteorological, human, environmental, economic, political, etc.).

In the case of an oil spill, the likelihood of an emergency situation is high enough and, therefore, a thorough analysis of the work conditions based on meteorological and technological factors is required. One of the most important technological problems during leakage and evaporation of petroleum is the occurrence of explosion hazardous areas. The main indicators for evaluating...
reliability and safety are the mass of evaporated oil and the intensity of evaporation, which are determined by the parameters of the heat balance of the evaporation process. Oil spilled during pipeline integrity loss or stored in emergency pits over the repair and recovery period has an open surface, evaporating into the atmosphere. Under the influence of solar radiation, nitrogen oxides and hydrocarbons can form photochemical oxidants - the components of photochemical smog that adversely affect not only the vegetation and animals, but also have a long-term effect on human health, depending on the intensity of the man-made stream. Nature and people are haphazardly experiencing the effects of all man-made physical and bio toxic factors in different combinations and as they accumulate.

Oil spilled during the accident or stored in the earth storage for quite a long time is exposed to solar radiation.

Since 1980 in TSOGU the authors have been conducting research to assess the thermophysical parameters of evaporation from an open surface during spills and storage of petroleum and petroleum products. The research results are taken as a basis for the development of a standard document approved by the Ministry of Fuel and Energy of the Russian Federation «Method of determining the damage to the environment in case of accidents on main oil pipelines», are published as monographs and textbooks, and also elaborated and implemented by Ryabov N.N. when developing «Recommendations on fire safety during repairs on the line part of main oil pipelines» in the Ministry of Internal Affairs.

Analysis of the existing literature shows that research on this question is quite often qualitative in nature. Thermodynamic conditions on the surface and the color of oil influence the degree of temperature rise in the upper layers of oil when exposed to direct solar radiation. It is known that the phenomenon of thermal radiation, as a process of energy propagation in the form of electromagnetic waves, by nature differs from conduction and convection and is accompanied by the thermal energy conversion into radiant, and conversely, the radiant energy - into thermal. The energy radiation is the result of complicated intra-atomic processes occurring due to the thermal energy. When heated, part of the body energy is inevitably transformed into radiant, the value of which is determined by the temperature. To date, a lot of literature was published, such as monographs, both translated and by Russian authors, where at a high scientific level many provisions of the heat and mass transfer and the associated mass exchange are investigated. The process of liquid evaporation is usually accompanied by the heat and mass exchange in boundary layers. To summarize the experimental and calculated data of these conditions, different systems of similarity numbers are applied. Accordingly, the results obtained by researchers vary. Available data for evaporation within their accuracy so far do not allow finding a clear influence of the mixture heterogeneity on the heat and mass exchange coefficient.

2. General information

Carriers of the radiant energy are electromagnetic waves with a wavelength of from a fraction of a micron (sunbeams) to many kilometers (radio waves). In physics, they are known as ultraviolet, visible - light, infrared rays and electromagnetic waves. Here, of the greatest interest are light and infrared rays with a wavelength of 0.4 to 40 microns that are absorbed by the bodies as their energy passes into thermal. If all the radiant energy passes through the substance, it is called absolutely transparent, or diathermic. Solids and liquids are virtually opaque (athermic) for heat rays.

Just as it is the case with the concepts of absorption and reflection. A white surface reflects well only visible (solar) radiation. In practice, this feature is widely used - white-colored cars tanks, reservoirs, where sun exposure is not desirable. Notably, white paint absorbs invisible heat rays just as well as the dark one.

It is known that neutral resins give color to petroleum. They possess an intense color and a strong coloring power. In fact, 0.005% of heavy neutral resin is enough to dye colorless gasoline straw yellow. According to V. M. Rybak, there is no strict relation between the color and the amount of resinous substances. For example, for oils of the same petroleum color can to some extent be a criterion for resin extraction, but when it comes to oils derived from other petroleum, we must
consider the fact that the resinous substances of different petroleum have different color. We should mention here that there are many different types of resin (oil, neutral, potential and actual), fundamentally different both in the physical and chemical properties. We can also single out carbamide, phenol-formaldehyde resins. From the optical standpoint, carbamide resins exhibit high lightfastness and are transparent, phenol-formaldehyde resins are colored brown or yellow which under the influence of sunlight can transform into yellow-brown or even black.

It is known that the opacity of petroleum layers is due to the presence of asphaltenes in it – the most macromolecular substances having a molecular weight in the range of 1600-6000. Asphaltenes do not melt, at high temperatures can form gases and hard-burning coke and are a hardly soluble component similar in the sense to various kinds of mechanical impurities.

It is expected that the color of oil will depend also on its content of fat, paraffin, ceresin, etc. Known methods for determining the color do not allow determination of the concentration coloring substances by comparing the color intensity of oil and a sample. The calorimeter practice suggests that petroleum and petroleum products color is not an additive property, and is close to the color of a darker component.

Thus, a color should be understood as a conditional oil quantity characterizing the color of oil and its degree of intensity compared to the color of standard solutions. It is also assumed that the petroleum emissivity factor \( \varepsilon \) depends on the color intensity. When analyzing the published literature, we haven't discovered any data on the emissivity factor of petroleum and petroleum products, although, for example, for sixteen different paints of all colors the emissivity factor varies from 0.92 to 0.96.

Under the direct solar radiation is meant radiation coming to the surface directly from the Sun at a radius of \( 5^\circ \). In the SI system, the radiation intensity is measured in (W/m²). This value is usually called the irradian. In actinometry, an equivalent term “radiation intensity” is used.

It is known that the free surface irradiane by the Sun determines the activity and position of the Sun above the horizon, as well as the state of the atmosphere. Solar activity according to the actinometrical observations from space remains constant for many years. Direct solar radiation \( J \) is measured by means of actinometers such as a Savinov-Janiszewski, AT-50 and others at actinometrical stations (AS). Distribution of AS in Russia is extremely non-uniform. For example, in the West Siberia region there is only one Omsk AS. Since data from actinometrical stations can be extended to the territory of up to 100 km, in some cases, the intensity of the direct solar radiation can be calculated using the average radiation intensity values, depending on the latitude, with an input probability of 0.95.

From the actinometrical standpoint, the state of the atmosphere is characterized by transparency, fluctuating from 0 to 100%; 0% - athermic atmosphere, 100% - diathermic. When the transparency of the atmosphere is about 0.8 or 80%, it means that 80% of the energy passes through the atmosphere, while the remaining 20% are dispersed. The transparency of the atmosphere depends on the cloudiness, which is the product of condensation and sublimation of water vapor. For engineering calculations, cloudiness may be quantified by various characteristics and features of cloudiness.

3. Mathematical modeling

If data on cloudiness is available, the average daily intensity of the direct solar radiation \( J_{\text{CP}} \), coming on a horizontal surface, can be found by:

\[
J_{\text{CP}} = \left[ \frac{K_{\text{1}}J_{1}\tau_{1-8}}{2} + \left( \frac{K_{\text{1}}J_{1}}{2} + \sum_{i=2}^{4} K_{i}J_{i} + \frac{K_{5}J_{5}}{2} \right) \tau_{0} + \frac{K_{5}J_{5}\tau_{5-8}}{2} \right]^{-1}\tau_{\text{DH}},
\]

where \( \tau_{1-8} \) - the time interval between the sunrise and the first observation, hour; \( \tau_{5-8} \) - the time interval between the sunset and the last observation, hour; \( K_{i} \) – the cloudiness observed during corresponding observation periods; \( J_{i} \) - the intensity of the direct solar radiation coming on a horizontal surface, W/m²; \( \tau_{\text{DH}} \) - the duration of daytime, hour;
\[ \tau_{DH} = \tau_3 - \tau_B, \tag{7} \]

where \( \tau_B \), \( \tau_3 \) - the sunrise and sunset times for a given location; \( \tau_0 \) - the time interval between observations.

Technical handbooks usually list common absorptive or emissive properties of surfaces, the use of which can lead to significant errors. In fact, the total absorption capacity depends not only on the nature of the substance, temperature and pressure, but also on the distribution of the incident radiation along the wavelength. Most of the known bodies have a monochromatic absorption capacity. It is to be recalled that a gray surface is a surface the absorptive (reflecting) capacity of which is the same for a large wavelength range. Common water absorbs 50-60% of radiation with wavelengths of about 6500-9000 nm, wavelengths of 5800-6300 - up to 80-90%, 3500-5500 - only 25-30%, 2800-3200 - more than 90% and 800-2300 - less than 15%. Thus, a wide spectrum of wavelengths (3000 nm) of the solar radiation, on one hand, and the limitations of the measuring equipment and the complexity of the petroleum composition, on the other, held back the research into the absorptivity of hydrocarbon fluids, such as condensate, petroleum, LPG and etc.

In order to establish the nature of the influence of solar radiation on the surface temperature the scientists in TSOGU conducted experimental studies. Samples of petroleum from various West-Siberian fields, kerosene and diesel fuel were placed in chemical vessels from 0.01 to 0.30 cm high and put under the sun and in the shadow. The amount of evaporated hydrocarbons \( \sigma \) was determined by weighing. We also observed changes in the temperature of petroleum and petroleum products with the free surface \( S = (0.003 \div 0.03) \text{ m}^2 \) and varying degrees of thermal insulation of the side walls and bottom. Checking the repeatability of the experimental data by the value \( \sigma \) using Cochran's criterion showed the dispersions homogeneity.

Figure 4 provides data on evaporation of Shaimskaya (curves 1, 3) and Surgutskaya (curves 2, 4) oils at the ambient temperature \( t_B = 29^\circ \text{C} \) and wind velocity \( \vartheta_B = 0.6 \text{ m/s} \). Curves 3-4 characterize evaporation “in the shadow”.

From these dependences we can see that the influence the solar radiation on the petroleum evaporation temperature is sufficiently large. So, over 9 hours of evaporation under the influence of solar radiation (curves 1-2) the value of losses \( \sigma \) was 2 times higher than during evaporation “in the shadow”. This is due to the fact that the surface temperature \( t_H \) “under the sun” of the Shaimskaya and Surgutskaya oils increased to 45 and 42\(^\circ\text{C}\), and the mean temperature of petroleum “in the shadow” was only 29\(^\circ\text{C}\). It should be noted that, when comparing the evaporation curves obtained when petroleum was exposed to the solar radiation with the evaporation curves of the same petroleum without the influence of the solar radiation (under condition that the temperatures are equal), they are fully identical. The change in temperature decreased with depth and almost stopped at a depth of 0.15÷0.20 m.

Analyzing the experimental data, we can note that the highly resinous Shaimskaya oil is slightly more exposed to solar radiation, although the difference and the surface temperature of the investigated oils are not significant. Thus, when determining the evaporative loss of oil from the open surface, the influence of direct solar radiation can be considered through the change in temperature in the daytime.

As a result of the regression analysis of numerous experimental data it was possible to obtain the formula for calculating the temperature of the upper layers of liquid

\[ t_{SD} = 0.5(t_{BD} + t_{AD})(16.94 \times 10^{-9} J_{CP}^{1.85} \tau_{BH} + 1), \tag{8} \]

where \( t_{SD} \) and \( t_{BD} \) – the surface temperature and the average temperature in the daytime, \( ^\circ \text{C} \); \( t_{BH} \) – the product temperature at the beginning of storage, \( J_{CP} \) – the average daily intensity of the direct solar radiation coming on a horizontal surface, \( \text{W/m}^2 \); \( \tau_{BH} \) – the duration of daytime, hour.
We can recommend using the obtained dependence in engineering design, for example, when determining evaporative losses and emissions of liquid hydrocarbons from the open surface. The relative error in the determination of the surface temperature of the oil in the formula (4) is about 20%, at the radiation intensity $J_{CP} \geq 190 \text{ W/m}^2$. The coefficient of multiple correlation was 0.94 and is with a confidence level of 0.95 by Student's test.

The following relationships are recommended to determine the surface temperature of petroleum and petroleum products:

$$t_s = t_H + 0.4 \div 0.6 (t_B - t_H),$$

and

$$t_s = 0.5 (t_B + t_H)$$

where $t_B$ and $t_H$ – the temperature of the air and the product, °C.

$$t_s = \frac{t_{SD} \tau_{DH} + t_{SH} (24 - \tau_{DH})}{24},$$

However, formulae (9) are obtained with respect to tanks and storage facilities, i.e. when the direct solar radiation does not reach the surface of the oil. Therefore, the average temperature of the open liquid surface per day should be defined as follows:

$$t_{SH} = 0.5 (t_{BH} + t_{HH}),$$

where $t_{SH}$ – the average temperature of the liquid surface at night, °C.

$$t_B = \frac{t_{BD} \tau_{DH} + t_{BH} (24 - \tau_{DH})}{24},$$
where \( t_{BH} \), \( t_{HH} \) – the temperature of the air and liquid at night, °C. The average daily ambient temperature can be determined by

\[
t_{BH} = \frac{24 t_B - t_{BD} \times \tau_{DH}}{24 - \tau_{DH}}.
\]

(12)

\[
t_{HH} = \frac{24 t_H - t_{HD} \tau_{DH}}{24 - \tau_{DH}}.
\]

(13)

Similarly to \( t_B \) we can write a formula for determining the average daily product temperature, therefore

\[
t_{SH} = \frac{24(t_B + t_H) - (t_{BD} + t_{HD})\tau_{DH}}{2(24 - \tau_{DH})}.
\]

(14)

Considering (12) and (13) after transformations, (11) can be presented as (14).

Using (14), the average daily temperature of the free surface can be determined as

\[
t_S = \frac{t_{SH} \tau_D + 12(t_B + t_H) - 0.5(t_{BD} + t_{HD})\tau_{DH}}{24}
\]

or

\[
t_S = \frac{12(t_B + t_H) + \tau_{DH} \left[ t_{SD} - 0.5(t_{BD} + t_{HD}) \right]}{24}
\]

(15)

After transformations using (8) we have

\[
t_S = 0.5(t_B + t_H) + 0.354 \times 10^{-9} JCP^{2.55} \tau^2_{DH} (t_{HD} + t_{BD}).
\]

(16)

or

\[
t_S = 0.5(t_B + t_H) + \frac{\tau_{DH}}{24} \left[ 0.5(t_{BD} + t_{HD}) \times 16.97 \times 10^{-9} JCP^{2.55} \times \left( \tau_{DH} + 1 \right) - 0.5(t_{HD} + t_{BD}) \right].
\]

When calculating the average daily temperature of the free surface of liquid hydrocarbons stored in the earth storage, we assume \( t_{HH} = t_{HDD} \) or determine it at a depth of: 2/3 from the fill-up height \( h \) at \( t_{HH} > t_B \), and 1/3 from \( h \) at \( t_{HH} < t_B \).

When petroleum and petroleum products spill on the water surface we can assume that \( t_{HH} \) is the water temperature measured at a depth of 0.5 m where the daily fluctuations of its value practically attenuate. In case the oil is on the soil surface, instead of \( t_{HH} \) we can use the soil temperature \( t_S \) measured by means of Savinov or Ivanov thermometers at a depth of 15 cm.

The air temperature at the time of sunset \( \tau_S \) can be taken as the average daily air temperature \( t_B \), allowing a sinusoidal temperature variation during the day. This calculation, of course, is characterized by significant errors (20÷30%), although in some cases it may be justified. For more accurate calculations, we recommend using the following formula:

\[
t_B = \frac{1}{N} \sum_{i=1}^{N} t_{Bi},
\]

(17)

where \( t_{Bi} \) – the temperature of a single measurement, °C; \( N = \frac{24}{\tau_N} \) - the number of measurements; \( \tau_N \) – the time between measurements, hour.

The average daily temperature of the petroleum surface when it is stored for a number of days can be determined by the formula similar to
\[ t_{SAV} = \frac{1}{n} \sum_{i=1}^{n} t_{Si}, \]  

where \( n \) – the number of storage days; \( t_{Si} \) – the average daily temperature of the petroleum surface determined by (16).

4. Summary
Experimental verification of the developed analytical relationships under production conditions in the study of the mass transfer process showed satisfactory statistical estimates. Models (8), (15) and (16) are adequate by Fisher’s test with a calculation error of 10±15% and the multiple correlation coefficient \( R=0.92÷0.95 \). The proposed methodological approach to determining the temperature of oil and its surface allows taking into account components of the heat balance and can be recommended for expert calculation of evaporative losses and emissions of hydrocarbons.

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