

Developing Mathematical Provisions for Assessment of Liquid Hydrocarbon Emissions in Emergency Situations

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Abstract. The paper reviews the development of methodology for calculation of hydrocarbon emissions during seepage and evaporation to monitor the reliability and safety of hydrocarbon storage and transportation. The authors have analyzed existing methods, models and techniques for assessing the amount of evaporated oil. Models used for predicting the material balance of multicomponent two-phase systems have been discussed. The results of modeling the open-air hydrocarbon evaporation from an oil spill are provided and exemplified by an emergency pit. Dependences and systems of differential equations have been obtained to assess parameters of mass transfer from the open surface of a liquid multicomponent mixture.

1. Introduction

Effective development of accident prevention techniques depends largely on goodness-of-fit a priori statistics and their treatment. Damage caused by the loss of pipeline integrity is determined, first of all, by the amount of flowing oil, its physical and chemical properties and the conditions that characterize the accident site, the volume of emissions. Knowing the characteristics and quantity of oil spilled, we can determine the strategy for accident response, necessary effort and resources, as well as prevent deterioration of the situation related to the spread of contamination.

Common methods of characterizing volatility of petroleum and petroleum products can be divided into two groups: experimental (direct and indirect) and theoretical. Direct methods include measuring the fluid volume before and after evaporation or calculating the vapor volume (mass). Direct determination of hydrocarbon emissions is extremely difficult, and in some cases impossible, especially for short-term storage encountered in emergency situations. For example, when determining emissions by measuring the oil level h_{B3} a basic rule of measuring technique is violated, according to which a small value must be obtained by direct measuring, rather than subtracting two inaccurate values.



a) offshore [1] b) onshore [2]

Figure 1. Petroleum evaporation during spills.



In the long run, indirect methods may become more commonly used, such as determining losses by a change in density, refractive index, hydrocarbon composition, saturated vapor pressure, etc. Calculations based on comparing samples are labor-intensive, technologically and practically hard-to-apply. For example, analysis of experimental data on evaporative petroleum losses obtained by various methods shows that their results, as a rule, are inconsistent due to large errors of the measurements and the inability to comply with the high requirements for sampling. It may be noted that to calculate emissions and losses of liquid hydrocarbons that are on the daylight surface adequate sampling is practically impossible.

2. Models and methods

According to classical concepts of the kinetic molecular theory of gases, diffusion is the process of distributing a substance from one medium to another. The process of liquid transformation into gas (vapor), occurring only on a free liquid surface, is referred to as evaporation. In both cases, distribution of the substance in the medium is due to a concentration gradient of the vapor. At a constant temperature, the rate of liquid W evaporation is directly proportional to the evaporation area S and the difference between the saturated vapor pressure p_s and p_i actually set at a given time and inversely proportional to the pressure in the system p_{am}

$$W = AS \frac{p_s - p_i}{p_{am}}, \quad (1)$$

where A – the coefficient of proportionality.

From (1) we can see that at the initial moment evaporation occurs at an infinite velocity, at its limit equal to the translational velocity of molecules, then it slows down and at $p_i = p_s$ stops. Evaporation from an open surface at $p_i = 0$ happens at a constant and maximal rate. The rate of gas space saturation largely depends on the state of the environment into which evaporation takes place. If there is an uneven temperature distribution in the system or external forces, such as electrical, act upon the system there occur thermal diffusion, pressure diffusion, electrodiffusion, etc., resulting in an uneven concentration distribution.

According to laws of C. Maxwell and J. Stefan, the mass amount dG of a substance, passing by diffusion per time $d\tau$ through the area S , perpendicular to the axis Y , is directly proportional to the diffusion coefficient D and the density gradient (concentration) $d\rho/dy$ in the direction of the diffusion path, i.e. concentration decreases. This is indicated by the sign (-) in (2):

$$dG = -D \frac{p}{p - p_p} \frac{d\rho}{dy} d\tau dS, \quad (2)$$

where D – the diffusion coefficient, m^2/s ; p_p – the partial vapor pressure; p – the total vapor pressure.

The known diffusion rate can be determined by Fick's law:

or via the pressure gradient

$$\omega = \frac{dM'}{d\tau} = -D \frac{dM}{dy} = -D \text{grad } C, \quad \omega = \frac{dM}{d\tau} = -D \frac{d\rho}{dy} = -D \text{grad } \rho. \quad (3)$$

where M' – the vapor amount per unit area, $M' = M/S$.

We know of a number of such equations derived on the basis of the classical kinetic theory of evaporation and diffusion, however, having been studied experimentally, they showed large discrepancies between the calculated and experimental data. Foreexample, in works covering experimental studies of the influence of airflow on evaporation of water at rest in an open container, the scatter of results amounts to 400%. Experimental studies conducted by M. N. Baranaev, M. V. Lourie, S. N. Sklyarenko, A. G. Kolesnikov, N. M. Mihailov, N. Carier and others produced dependences in which the velocity index ranged from 0.3 to 1.0. Theoretical and experimental studies of the losses of petroleum and petroleum products from evaporation in surface and underground tanks

were carried out in the works of Abuzova F.F., Bunchuk V.A., Novoselov V.F., Konstantinov N.N., Fathiev N.M., Dushin V. A. et al.

Sklyarenko S.N. and Baranaev M.N. note that the reason for discrepancies in the values are due to the difference in flow conditions in which the evaporation takes place. Increasing the speed of the airflow from minor (where evaporation is determined by the rate of vapor molecular diffusion) to turbulent (where convective currents take precedence in evaporation) leads to a varying evaporation rate of the substance. Thus, the transfer of vapor from the liquid surface to the environment is caused by pure molecular diffusion, as well as convection. It follows that when characterizing mass transfer we must consider two types of evaporation: *static* and *dynamic*.

According to A. V. Nesterenko, thickness of the boundary layer can be expressed by the vapor density ρ , i.e., $\delta = \rho D$. However, δ also depends on the nature of the vapor-air medium flow near the surface. Evaporation processes are caused not only by the vapor concentration, but also by different effects, such as temperature, molecular movement of vapor and air in the boundary layer, etc. During evaporation of substances with a molecular weight substantially less than the molecular weight of air, convection currents will be directed upwards, and for substances with a molecular weight greater than the molecular weight of air - downwards. By this convection currents complicate evaporation.

A small vapor concentration C_s , corresponding to saturation, will occur by the evaporation surface in a relatively thin, so-called boundary layer δ . After the boundary layer, the vapor concentration decreases with increasing distance from the evaporation surface. As various thermodynamic conditions are possible on the surface of the substance and in the environment, it is almost impossible to accurately determine the boundary layer thickness δ .

It becomes clear why the evaporation rates observed experimentally exceed those obtained by calculation using the formula of "free" diffusion, for example

$$g_x \frac{\partial C}{\partial x} + g_y \frac{\partial C}{\partial y} + g_z \frac{\partial C}{\partial z} = D \left(\frac{\partial^2 C}{\partial x^2} + \frac{\partial^2 C}{\partial y^2} + \frac{\partial^2 C}{\partial z^2} \right) \quad (4)$$

Integrating this differential diffusion equation with partial derivatives in the space with complex boundaries gives many different solutions. In most cases, such as for a stationary process and a three-dimensional diffusion field, it is almost impossible to find a solution satisfying the differential diffusion equation and the single-valuedness condition. Simplification, however, distorts the mechanism of the phenomenon.

Indeed, evaporation causes a loss of petroleum products mainly of light ends, whereby fluid "becomes heavier" changing mass transfer in different ways. To calculate evaporative hydrocarbon emissions that can reach 40% of the weight, of particular importance is the diffusion coefficient D (*molecular, turbulent*)

Data on changes in D of petroleum at various levels of evaporative losses in Russian and foreign literature are clearly insufficient. In practice, diffusion coefficient is determined by the computational-experimental method of A. S. Irisov using a special evaporator at the liquid-gas phase ratio of 4:1. A number of diffusion coefficient values have been produced in Ufa State Petroleum Technological University by F. F. Abuzova, V. F. Novoselov, V. N. Chernikin and V. A. Martyashova primarily for commercial petroleum products. When temperature changes within the range of 10-40°C, the coefficient changes within a narrow range (25% of the mean value 20.5%). According to the authors, even for gasoline of the same grade this coefficient depends on the source petroleum and processing methods applied at the refinery.

From the analysis of works it follows that the diffusion coefficient decreases with increasing molecular weight of hydrocarbons and increases significantly with increasing temperature. The difference in the diffusion coefficients of various hydrocarbon vapors diminishes with increasing molecular weight. In case of equal molecular weight, arenes have the largest values of D , and cyclanes – the smallest. Alkane hydrocarbons occupy an intermediate position.

Also known is the effective diffusion coefficient D_e , which is used for formal coordination of the experimental data with the theoretical predictions. D_e describes intensification of petroleum vapor transport due to evaporation.

When, for instance, a reinforced concrete storage tank ZhBR–10000 containing petroleum at a higher temperature is emptied, D_e 0-80 times exceeds the molecular diffusion coefficient, and when it is filled – by 40%. Experimental studies of the molecular diffusion coefficients, depending on the temperature and vapor pressure, for gasoline, Samotlor and Ust-Balyk oil, etc. allowed us to determine the value of evaporative losses with an error of 25 - 60% increase.

Loktev V.M. noted that when gasoline grades B-70 and AI-93 are evaporating diffusion coefficients of vapors in the air change significantly. He also proved that diffusion coefficients of gasoline of the same grade but measured in different years of production vary in value.

Based on extensive research, Irisov A.S. determined that when Re increases the influence of D is not proportional to the evaporation rate but raised to the power $m=2/3$, i.e. $D^{2/3}$, in other words, becomes smaller.

As far as oil is concerned, differences in the hydrocarbon composition are more significant, resulting in a drastic difference in the diffusion coefficients. Irisov A.S. claims in his works that the decisive factor in determining the rate of evaporation of petroleum products is saturated vapor pressure, and the diffusion coefficient has only an additional effect. Spalding D.B. expresses a similar view after studying diffusion of various mixtures of gases with air. The author notes that the value of the diffusion coefficient is not very sensitive to changes in the composition for binary mixtures, even when compared to the influence of viscosity or molecular weight.

Thus, given the very limited data on the diffusion coefficient of petroleum and petroleum products and a considerable complexity of its determination when calculating oil evaporation losses from an open surface, it is necessary to carry out calculations with great care.

From the analysis it follows that no matter whether the calculated ratios of mass transfer are based on experiment or mathematical analysis, they contain mass transfer coefficients from the open surface of multicomponent hydrocarbon fluids and a large number of dependent factors, which prevents the experimental data from being adequately summarized.

Published data (within their accuracy) on evaporation of multicomponent substances do not allow discovering a clear influence of the mixture heterogeneity on the mass transfer coefficient and the rate of evaporation from the open surface. The methods used for calculating losses based on the determination of evaporation coefficients and mass transfer from the surface of petroleum and petroleum products describe the process of mass transfer only in closed vessels.

A data bank of coefficients of diffusion, mass transfer, thermal conductivity, and so on is required created on the basis of extensive experiments under a wide range of conditions. To date, this type of extensive research has not been carried out.

An alternative solution to the problem of calculating evaporative emissions may be adapting methods based on the equations of state of multicomponent mixtures to the given conditions.

3. Mathematical modeling

According to Raoult's law for the mixture of liquid hydrocarbons, the saturated vapor pressure p_s depends upon the saturated vapor pressure of the individual components and the molar concentrations. It is equal to the sum of pressures of the mixture components that they would have if each of them occupied the entire volume of the mixture at a given temperature, i.e. the sum of partial pressures.

From the combined Dalton-Raoult law, we can draw an important conclusion - in equilibrium, the partial pressure of any component of the mixture in the vapor phase is equal to the partial pressure of that component in the liquid, from which

$$p_{Si}/p_S = y_i/x_i = k_{pi} = const$$

or

$$p_{Si} = k_{pi} p_S \quad u y_i = k_{pi} x_i, \quad (5)$$

where p_{Si} is the saturated vapor pressure of a pure component; y_i and x_i is the molar concentration of a component in the vapor and liquid phases.

Coefficient k_{pi} is known as *the equilibrium constant* (or phase equilibrium constant), which under conditions of the equilibrium state (5) allows, for example, finding the gas phase composition by a known fluid composition, and vice versa. If $k_{pi} > 1$, then this component will have a higher concentration in the vapor phase than in the liquid, and vice versa.

Besides the phase equilibrium equation (5), during the evaluation of the phase state we can use (6) called the flash evaporation start equation and characterizing the equilibrium system with a small amount of vapor or (7), characterizing the system in the vapor phase with a small amount of liquid.

When forecasting the material balance of multicomponent two-phase systems (or the concentration of components in different phases) k_{pi} are commonly used when

$$\sum k_{pi} x_{i0} = 1 \quad (6)$$

$$\sum \frac{y_i}{k_{pi}} = 1 \quad (7)$$

pressure and temperature (initial t_{H0} and final t) are given and the molar concentration of the i^{th} component is known, for instance, in the liquid x_{i0} or gaseous y_i state.

For any component, the number of moles in two phases is determined as a sum of N_i^g and N_i^l , i.e. $N_i^0 = N_i^g + N_i^l$. Hence, the molar concentration:

$$x_{i0} = y_i g + x_i l, \quad (8)$$

where g and l – the numbers showing the proportion of the total number of moles in the gaseous and liquid state, respectively ($g+l=1$). In practice, g is calculated using the successive approximation method that is easily implemented by means of a personal computer. It is assumed that $\sum x_i = 1$, which follows from (7).

$$x_i = \frac{x_{i0}}{k_{pi} + (1 - k_{pi}) l}, \quad y_i = \frac{k_{pi} x_{i0}}{k_{pi} + (1 - k_{pi}) g}. \quad (9)$$

Considering that $y_i/x_i = 1$, for the i^{th} component concentration in the liquid and gaseous phases we can use the following expressions:

The equilibrium compositions of a two-component system are much easier to determine:

a) for the liquid phase:

$$x_1 = \frac{1 - k_{p2}}{k_{p1} - k_{p2}}; \quad x_2 = \frac{k_{p1} - 1}{k_{p1} - k_{p2}}; \quad (10)$$

b) for the gaseous phase:

$$y_1 = \frac{k_{p1}(k_{p2} - 1)}{k_{p2} - k_{p1}}; \quad y_2 = \frac{k_{p2}(1 - k_{p1})}{k_{p2} - k_{p1}}. \quad (11)$$

The processes of open or flash evaporation of liquid multicomponent mixtures are widely used in laboratory and industrial practices and usually involve the use of the iteration method for calculations. To develop a technique for calculation of emissions of liquid multicomponent hydrocarbon mixtures from the open surface we conducted the analysis of existing methods of mathematical modelling of mass transfer. It showed that open evaporation processes are non-stationary and are described by a system of differential algebraic equations. Flash evaporation processes are stationary and are described by a system of ordinary nonlinear algebraic equations.

Let us consider the process of open evaporation of hydrocarbons from an oil spill or, for example, an emergency pit illustrated in Figure 2. The vessel has the shape of a truncated pyramid with an angle of sidewalls inclination α and filled with oil to different heights h_{lev} . The amount of initial liquid M can be determined by

$$M = \frac{\rho}{3} (S_1 + \sqrt{S_1 S_2} + S_2) h_{lev}, \quad (12)$$

where ρ - the density of the petroleum; S_1, S_2 - the areas of the vessel base and the free petroleum surface.

To determine the vapor flow M_u let us build a system of equations of heat and material balances and of the phase state.

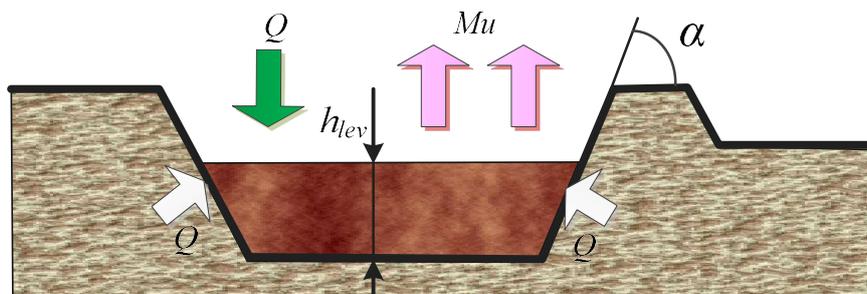


Figure 2. Diagram of an emergency pit.

For the isobaric process, an infinitesimal amount of heat dQ can be represented as a total differential of a certain value J , called enthalpy (formerly known as heat content), i.e.

$$dO = dJ = C_p dt, \quad (13)$$

where C_p - the isobaric heat capacity.

It is known that when temperature changes from 0 to 50°C the heat capacity of gasoline varies from 1.93 to 2.28 kJ/kg·K, and that of oil - from 1.80 to 2.52 kJ/kg·K. With sufficient accuracy, the heat capacity of petroleum and petroleum products can be determined analytically by Crego's formula:

where ρ_{293} - the density of the petroleum product, kg/m³.

When determining the isobaric heat capacity of the condensates of the Urengoiskeye field, we can use Mustafayev's formula:

$$C_p = \frac{31,56}{\sqrt{\rho_{293}}} (762 + 3.39T), \quad (14)$$

$$C_p = 3.3909 - 1.6747 \cdot 10^{-3} \rho_T [\text{kJ/kg} \cdot \text{degree}]. \quad (15)$$

A change in the heat capacity depending on the boiling point T_K , of the condensate with the density $\rho_K = 650 \div 720$ kg/m³ can be characterized by the following dependence proposed by TSOGU:

$$C_p = 1030.8 + 4.50 T_K, \quad [\text{J/kg} \cdot \text{degree}] \quad (16)$$

for a mixture of NGL with a condensate ($\rho_K = 550 \div 590$ kg/m³):

$$C_p = 1060.4 + 4.796 T_K, \quad (17)$$

for a stable condensate ($\rho_K = 730 \div 770$ kg/m³):

$$C_p = 887.0 + 3.9460 T_K, \quad (18)$$

where T_K - the average boiling point of the condensate, K.

The enthalpy is a state parameter of a thermodynamic system. Its change in the isobaric process equals, as is evident from (13), the amount of heat obtained by the system. Of practical interest are changes in the enthalpy rather than its absolute values, i.e. the concept of enthalpy, just as the concept of heat, refers to the process rather than the state. Its physical meaning can be summarized as follows: the enthalpy of any thermodynamic system is the total energy of the system. If overheating of petroleum product vapors is not required we can determine the enthalpy of saturated vapors that, at the given temperature, corresponds to the amount of heat required for heating 1 kg of liquid (petroleum product) from 0 °C to the given temperature and its evaporation at the same temperature. This value is

known as the *total heat of evaporation* and equals the enthalpy of the liquid at the boiling point plus the latent heat of evaporation.

Enthalpy is calculated for liquid hydrocarbons and their vapors. For practical calculations of enthalpies of liquid petroleum products at pressures close to atmospheric and different temperatures t we can use known nomograms or, for example, dependences developed by Illembitov R. I.:

$$h = \left(\frac{4.187}{\sqrt{\rho_4^{20}}} \right) (0.3886t + 0.00045t^2), \quad (19)$$

for petroleum vapors:

$$I = 4.187 \left[(139 - 62.92\rho_4^{20}) + (0.4576 - 1.43\rho_4^{20})t + \right. \\ \left. + (503 - 57.2\rho_4^{20})10^{-6}t^2 - 35(1 - \rho_4^{20})^3 \right], \quad (20)$$

where ρ_4^{20} – the relative density of the substance at 20°C.

The enthalpy of liquid hydrocarbon mixtures is virtually independent of the pressure and can be determined by the value of the enthalpy of individual components using the rule of additivity

$$I = \sum k_{pi}(t) x_i I_i(t) \quad (21)$$

For vapor mixtures, such calculation introduces some error, although in some cases it is feasible, for example, when characterizing the processes of open or flash evaporation of liquid multicomponent mixtures widely used in laboratory and industrial practices

$$h = \sum x_i h_i(t) \quad (22)$$

Thus, considering equations (6)÷(19) mass transfer from the exposed surface of the liquid multicomponent mixtures can be characterized by the following system:

$$\frac{d}{d\tau} M = -M_u; \quad (23)$$

$$\frac{d}{d\tau} x_i = \frac{M_u}{M} (1 - k_{pi}) x_i; \quad i = \overline{1, n}; \quad (24)$$

$$\frac{d}{d\tau} (Mh) = -M_u I + c_p (t - t_{HO}) M + \theta; \quad (25)$$

$$\sum k_{pi} x_i = 1 \quad (26)$$

with initial conditions at $\tau=0$

$$M = M_0; \quad x_i = x_{i0}; \quad \sum k_{pi} x_{i0} = 1, \quad (27)$$

where τ - the time of evaporation, s; M – the molar amount of evaporated liquid; M_u – the molar vapor flow; $\{x_i\}$ – the concentration of components in the liquid phase; I - the enthalpy of the vapor mole, J/kg; h - the enthalpy of the evaporated mixture mole, J/kg; $\{c_p(t_{HK} - t_{HO})M + \theta\} = Q$ - the heat flow supplied to the evaporated mixture, J/s; t_{HK} , t_{HO} – the initial and the final temperature of the mixture; θ - the heat flow required to transform M_u into vapor.

The system of ordinary differential equations (23)÷(26) contains $(n+3)$ equations and $(2n+5)$ variables: k_{pi} , $\{x_i\}$, M , M_u , t_{HK} , Q . Therefore, to carry out accurate calculations of mass transfer it is enough to bring the resulting system in line with the number of variables. If the a priori information on the deterministic values k_{pi} , t_{HO} , and Q is available, solving the system with determining $\{x_i\}$, M , M_u and t_{HK} is not particularly difficult. The authors obtained a solution of the system of differential

equations of mass transfer by a Runge-Kutta method, and proposed a technique of determining the constants of phase equilibrium $k_{pi}\{x_{ij}\}$. The research results produced in TSOGU are taken as a basis for the development of a standard document and are published as monographs and textbooks.

4. Summary

Thus, the developed models and technique for calculating parameters of multicomponent substance mass transfer and flash evaporation processes as applied to petroleum and petroleum product spills with the deterministic composition allow us to assess the quantity of spills and liquid hydrocarbon losses during their evaporation from an open surface.

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