Mathematical model describing the rate of evaporation of high-temperature petroleum products used in the oil and gas industry

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Abstract. Within the framework of the study, the process of evaporation of heated high-temperature oil products was studied, the results were used to determine the calculated values of the mass of vapors formed during the evaporation of spills of liquids heated above the design temperature. The result of the study was the development of a theoretical model based on the Stefan formula describing the rate of evaporation. This made it possible to establish that when heating high-temperature organic compounds form explosive vapor-air mixtures that pose a fire hazard.

1. Introduction
The share of oil and gas revenues in the budget of the Russian Federation in the last ten years has fluctuated from 29 to 51%, and most of them come from the sale of crude oil abroad. Moreover, this figure does not include general taxes on the oil industry - value added tax, property tax and others. In 2018 - 2019, oil and gas revenues in the budget exceeded 40%, but in 2020, apparently, this figure will greatly decrease due to the fall in energy prices. In the first half of 2020, it was 29.3% [1].

The figures clearly show that it is possible to talk a lot and correctly about the need to get away from oil dependence, but it is difficult to deny the enormous importance of the industry for the Russian economy. The mere fact that it employs more than half a million people, and it serves as a driver for the development of heavy engineering, shipbuilding, chemical industry and digital technologies make it the most important industry for the country.

Reserves are currently being developed that were previously considered unavailable. The most striking example is the giant Priobskoye field with recoverable reserves of 2.4 billion tons. Until a certain point, it was believed that the field was too difficult for industrial development, and now it gives more than 4% of all oil produced in Russia [2].

Work efficiency has increased. The history of the Romashkinskoye field in Tatarstan is indicative here. Its recoverable reserves are estimated at 3 billion tons. At the same time, it has been industrially developed since the 50s of the last century and it is believed that there will be enough oil in it until 2060. For several decades, the field has served as a testing ground for testing the latest technologies in the field of subsoil exploration, well drilling, oil production, which then find wide application not only in our country, but all over the world.
Development of fields began in Eastern Siberia and the Far East. Moreover, the subsoil of the region has not yet been explored even by half, but already now it produces more than 12% of all oil produced in the country. And here unexpected discoveries may still take place [2, 3].

Oil refining deserves special words. The depth of oil refining (the ratio of the volume of oil refined products to the total volume of oil spent for this) has grown from 60% in the 80s of the last century to 82.7% in 2019.

The entire industry now faces new challenges. The resource base is deteriorating - the number of hard-to-recover reserves (TRIZ) is growing, for the development of which you need to create your own technologies. Production goes to ever deeper and more difficult to access subsoil horizons, geographically shifting to the Arctic zone, including the shelf. But at the same time, the volumes of oil production in Russia have been at a level above 500 million tons per year for 10 years without any obvious tendencies to decrease in the future [4].

In addition, global warming, in the form of degradation of permafrost, also affects the state of the objects of protection of the oil and gas industry. This factor is almost not taken into account today in the capital construction of new facilities, and especially in the repair and reconstruction of existing ones. And this must be given special attention when considering such projects. A typical example of an environmental disaster is a federal emergency that occurred on May 29, 2020 when a diesel fuel tank was depressurized at TPP-3 in Kayerkan. This is one of the largest spills of oil products in the Arctic zone in history, posing a threat to the ecosystem of the Arctic Ocean. Do not forget that the oil and gas industry is explosive and fire hazardous, constantly changing in order to please modern trends. Consequently, the provision of fire safety in this industry must reach a new modern level [5, 6].

2. Development of a theoretical model for calculating the mass of vaporization of flammable liquids

It should be noted that low ambient temperatures prevail on the territory of the Russian Federation, especially in places where oil and oil products are produced and processed. Therefore, when conducting various technological processes (transportation, pumping, storage), heated flammable liquids are used (for example, as a heat carrier): armotherm, mobitherm, definitional mixtures and other high-temperature organic heat transfer fluids. A feature of such flammable substances is their ability to form vapor-air mixtures and explosive aerosols inside technological equipment during normal operation and during emergency emissions [7, 8].

Within the framework of the study, the process of evaporation of heated high-temperature oil products was studied, the results were used to determine the calculated values of the mass of vapors formed during the evaporation of spills of liquids heated above the design temperature. The result of the study was the development of a theoretical model based on the Stefan formula describing the evaporation rate (1):

$$W = \beta \cdot \frac{p}{RT} \cdot \ln \left(\frac{P - P_s}{P - P_0}\right)$$  \hspace{1cm} (1)

where, $N_u$ – Nusselt test;
$D$ – molecular diffusion coefficient;
$d$ – the characteristic size of the evaporation center;
$P$ – atmospheric pressure, mPa;
$P_0$ – partial pressure of liquid vapors far from the surface, mPa;
$R$ – universal gas constant, $(8.31 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1})$;
$T$ – temperature at the “air-liquid” interface, K;
$P_s$ – partial pressure of saturated vapors at the surface of liquid evaporation, mPa;
$\beta$ - mass transfer coefficient calculated by the formula (2):

$$\beta = \frac{N_u \cdot D}{d}$$  \hspace{1cm} (2)
Let us represent the specific gravity of a combustible liquid in the form of the formula (3):

\[ m_{vap} = \int_{0}^{\infty} W_{vap} \cdot dt \]  

(3)

If for calculations we take the average temperature of the combustible fluid of the coolant, in accordance with the Newton – Richmann law of heat transfer, and also use the Clausius – Cliperon equation, then the dependence of diffusion on temperature for the specific mass of the evaporated liquid will take the form, formula (4):

\[ m_{vap} = \frac{a \cdot \sqrt{M \cdot P_s \cdot C_l \cdot m_l}}{F \cdot H_{vap}} \left[ 1 - \exp\left( -b \cdot \frac{H_{vap}}{R \cdot C_l \cdot m_l} \right) \right] \]  

(4)

where \( M \) – molar mass of liquid, g/mol; 
\( P_s \) – saturated vapor pressure at the initial evaporation temperature, mPa; 
\( C_l \) – specific heat capacity of the liquid at the initial temperature of evaporation, J/kg\( \cdot \)K; 
\( m_l \) – mass of liquid released during an accident, kg; 
\( H_{vap} \) – specific heat of vaporization of the liquid at the initial temperature of vaporization, kJ/mol; 
\( F \) – calculated area of evaporation, m; 
\( T \) – evaporation time of the heated liquid, s; 
a and b – calculated coefficients 0,012 и \(-2,9\cdot10^{-6}\) respectively.

The relative permissible deviation of the mass of the evaporated coolant can be determined by the formula (5):

\[ m_{vap} = 0,02 \cdot \frac{\sqrt{M \cdot P_s \cdot C_l \cdot m_l}}{L_{vap}} \]  

(5)

where, \( M \) – molar mass of liquid, g/mol; 
\( P_s \) – saturated vapor pressure at the initial evaporation temperature, mPa; 
\( C_l \) – specific heat capacity of the liquid at the initial temperature of evaporation, J/kg\( \cdot \)K; 
\( m_l \) – mass of liquid released during an accident, kg; 
\( L_{vap} \) – specific heat of vaporization of the liquid at the initial temperature of vaporization, kJ/mol.

It follows that explosive concentrations will be formed not only when using oil products in the technological process, but also when the heating systems are depressurized, which also poses a danger to personnel.

**Table 1.** Calculated values of the mass of evaporation for heat transfer fluids.

| Substances name | M\(\sqrt{M}\) g/mol | \(P_s\) MPa | \(C_l\) J/kg\( \cdot \)K | \(m_l\) (cons’t) kg | \(L_{vap}\) kJ/mol | \(m_{vap}\) kg |
|-----------------|---------------------|-------------|----------------|-----------------|----------------|----------|
| Dinyl \(C_{12}H_{10}O\) | 170/13 | 1.5 | 1591 | 300 | 48.2 | 38.6 |
| Ditolylmethane \(C_{15}S_{16}\) | 196/14 | 0.4 | 1553 | 300 | 33.18 | 15.7 |
| Mobilterm \(C_{12}H_{10}O\) | 170/13 | 0.1 | 1599 | 300 | 48.2 | 25.8 |
| Terminol \(C_{18}H_{14}\) | 230/15 | 0.7 | 1552 | 300 | 39.93 | 27.3 |
| Marloterm \(C_{10}H_{4}O\) | 108/10 | 0.1 | 1560 | 300 | 50.48 | 23.2 |
### 3. Conclusion

Modern conditions of economic and technical development make it possible to talk about constantly changing criteria for ensuring fire safety in the oil and gas industry. What is connected with the emerging sources of emergencies.

Thus, the result of the study was the development of a theoretical model based on the Stefan formula, which describes the rate of evaporation of high-temperature organic compounds. To test the simplified formula, we calculated the mass of evaporated vapors for a number of coolants. The obtained values prove the possibility of the formation of air-vapor mixtures, which pose an additional hazard to the facilities of the oil and gas industry.

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