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ANALYSIS OF THE CONDITIONS OF PHASE EQUILIBRIUM AND INFLUENCE OF THE UNITED HEAT AND MASS TRANSFER ON THE EFFECTIVENESS OF SEPARATION IN THE INERTIAL-FILTERING SEPARATOR

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Abstract. In this paper the basic thermodynamic parameters that have the greatest impact on the efficiency of the separation processes of gas-liquid mixtures and phase equilibrium in such systems are considered. The general characteristics of separation processes based on phase equilibrium are given. The main approaches to the calculation of phase equilibrium and coupled heat are analyzed. Possible ways of gas separation technology improvement and development are explored.

Keywords: modeling, equilibrium, gas-liquid mixture, critical parameters, phase equilibrium constant, thermodynamic parameters, condensation.

1. Introduction

Hydrocarbon gases mined from the oil fields depths are saturated with water vapor. The crude gas includes a large number of liquid drops, consisting of mineralized water and gas condensate, usually in the amount of 30–40 g/m³ and sometimes 200–800 g/m³. Therefore, this gas-condensate mixture before serving in pipelines or production lines is treated, including the separation of moisture, solids and hydrocarbon condensate.

The aim is to analyze the thermodynamic properties of gas condensate mixtures and determine the conditions of phase equilibrium and mechanisms of formation of such systems for further deep study, development and process improvement of inertial-filtration separation.

In the case of an infinite mass of vapor in the system provided that there are phase transitions and the

initial gas temperature is less than the drops surface temperature, then there is no limit equilibrium, as in this case, the drop will be infinitely increased by condensation. If the initial temperature of the gas is over the drops surface temperature, the drops evaporate completely and install a homothermal gas temperature. But if there is some finite mass of vapor, the limit equilibrium always exists. It is determined by the initial state, after solving the system of equations of mass, energy, phase equilibrium, and state conservation.

2. Results and Discussion

2.1. Analysis of the Basic Thermodynamic Parameters Affecting the Gas-Liquid System

Hydrocarbon fractions C₃₊ escaped from the natural and accompanying petroleum gas (topping) is usually carried out using moderate cold temperature at the low-temperature condensation and separation units (STC and NTS) and also using the devices which change system thermodynamic parameters (pre-condensing units (PCU). These devices are choke, heat transfer device, or turbo-expander. Liquid phase (fog) formation in the PCU is based on the gas mixture adiabatic expansion, when mixture volume increases, steam pressure and temperature decreases, and these processes take place simultaneously because expansion occurs due to internal gas energy [1].

When gas-liquid mixtures pass through these devices pipeline phase equilibrium is broken. Therefore,

drops nucleation takes place as a result of united heat and mass transfer – condensation and evaporation. Thermodynamic phase equilibrium disturbance is caused by pressure p and temperature t changes.

The most interesting are such values of these parameters at which liquid droplets enlargement takes place, as it eases their separation from gas in the separator according to the main mechanisms of inertial separation when only hydrodynamic processes take place. Individual components of the hydrocarbon liquid mixtures have excellent critical parameters (in particular, critical temperature and pressure), so when thermodynamic characteristics of the system are changed (and particularly when pressure increases and temperature decreases), separate components can condense. It has positive impact on the effectiveness of inertial-filtering separation [2].

By lowering the system temperature steam pressure of saturated components decreases so the system becomes non-equilibrium and some part of the components transfer to the liquid phase in the form of monodispersed drops that means partial condensation takes place in the gas liquid mixture. To reach condensation of separate gas liquid mixture component its partial pressure should correspond to the steam pressure at a given temperature. At that, condensed droplets will be in equilibrium with the gas -liquid mixture.

Hence, for each component of the gas-liquid system one can record the condition of its equilibrium distribution between phases:

$$K = y_i / x_i \quad (1)$$

where K – phase equilibrium constant of the separate component; y_i – molar fraction of the i^{th} component in the gas phase; x_i – molar fraction of the i^{th} component in the liquid phase.

Since sum of the components in gas and liquid phases must be equal to unity, taking into account equation (1) we can write [2, 3]:

$$\sum_{i=1}^n y_i = 1 = \sum_{i=1}^n \frac{1}{V_i} \cdot \frac{K_i \cdot z_i}{K_i + L_i / V_i} \quad (2)$$

$$\sum_{i=1}^n x_i = 1 = \sum_{i=1}^n \frac{1}{V_i} \cdot \frac{z_i}{K_i + L_i / V_i} \quad (3)$$

where V – molar fraction of the gas phase in the mixture; L – molar fraction of the liquid phase in the mixture; z_i – molar fraction of the i^{th} component in the mixture.

For determination of actual systems and their equilibrium constants one can use fugacity coefficient, which binds fugacity and properties of the system to be identified.

Gas and liquid phases fugacity coefficients [2]:

$$j^G = f_i^G / P \cdot y_i \quad (4)$$

$$j^L = f_i^L / P \cdot x_i \quad (5)$$

where f^G and f^L – fugacity of the gas and liquid phases, respectively.

Using formulas (4) and (5) we obtain gas-liquid systems equilibrium equation:

$$j^G \cdot y_i = j^L \cdot x_i \quad (6)$$

Thus, the phase equilibrium constant can be determined by fugacity coefficients:

$$K_i = j^L / j^G \quad (7)$$

The same condensation level of the initial gas fluid mixture components can be reached using different combinations of temperature and pressure. Condensation intensity does not depend in direct proportion on the changes of these parameters. Thus in the low-pressure zone condensation intensity can change even when pressure fluctuation is insignificantly small. However, if pressure growth continues condensation intensity reduces. Temperature changes have the same influence. If temperature is reduced to some specified level condensation increases intensively. If temperature is lower than this specified value condensation rate decreases.

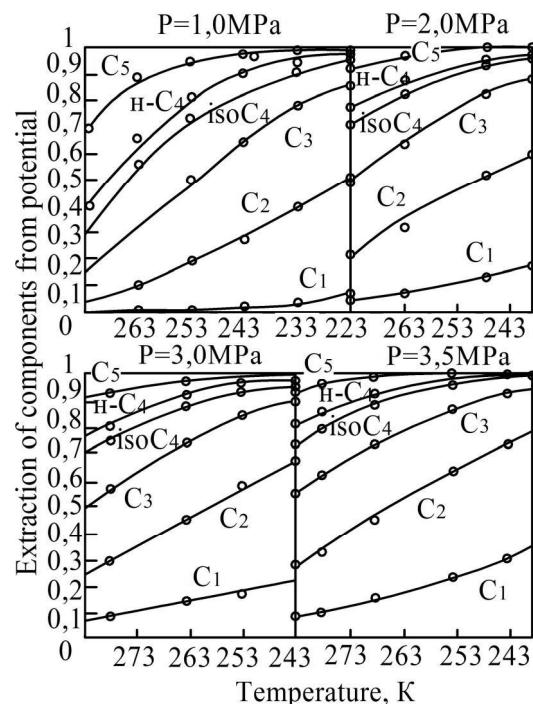


Fig. 1. Dependence of gas components removal on temperature and pressure

Fig. 1 [4] shows the dependence of gas components removal on temperature and pressure fluctuations. Studying the picture one can see that propane volume removed under conditions pressure (MPa) / temperature (K) equal to 1.0 / 233 and at 3.5/263 is approximately the same but the level of extracted light gas components in the first case is 1.5 times higher than in the second one.

It proves the fact that when pressure during condensation increases selectivity of condensation components decreases. Therefore, to get pure separate gas components or narrow fraction of hydrocarbons it is necessary to provide moderate pressure (1–2 MPa) and low temperatures (253–243 K) in the inertial-filtering separator. One can reach it by carrying out separation and condensation processes simultaneously in one device – separator-condenser, which can be used as an alternative apparatus to traditionally used prior condensation devices.

2.2. Analysis of the Main Phase Equilibrium Determination Methods

Phase equilibrium constants depend on the system thermodynamic parameters and on the phases composition. Thermodynamic properties of petroleum and natural gas as well as their components differ significantly from the properties of the ideal gas. One can see it clearly in the case of low temperatures and high pressures. Therefore, there are many equations of state to determine and describe properties of the hydrocarbon systems. Among the most widely used equations of state one can call Redlich-Kwong equation, modified by Souv, Peng-Robinson equation, Benedict-Webb-Rubin equation, modified by Starling [3, 4]. Each equation of state has its advantages and disadvantages. These equations are solved using the method of successive approximations; choosing dew point temperature at the corresponding partial pressures of the components. After all, it is necessary to achieve the conditions of Eqs. (2) and (3).

Graphical methods are very accurate for manual calculations of phase equilibrium constants. The most simple and accurate one is NGPA method [4].

Using this method phase equilibrium constants of hydrocarbon are determined by a series of graphics depending on the temperature, system pressure, and convergence pressure. In these graphics, the abscissa axis represents system pressure values and the vertical axis – phase equilibrium constant of a particular system component. In these coordinates there are isotherms which converge at one point when $K = 1$ and at pressure equal to the system convergence pressure. For different mixtures having the same pressure convergences

equilibrium constants of identical components have the same value at the same temperatures and pressures.

Therefore, convergence pressure is used as a parameter that shows the mixture composition influence on the phase equilibrium constant.

Using the obtained phase equilibrium constants, composition of the equilibrium liquid phase is calculated according to the equation:

$$\sum_i x_i^* = \sum_i \frac{c_i}{1 + e(K_i - 1)} = 1 \quad (8)$$

where e – molar fraction of the steam phase.

Convergence pressure is determined by Hadden method [4]. By this method liquid multicomponent phase is figuratively represented as a binary system consisting of a light component and hypothetical heavy component, characterized by bulk critical temperature and bulk critical pressure of all mixture components except the light one.

Convergence pressure is defined as a critical pressure of this pseudo-binary system at the system temperature at the critical curve of this pseudo-binary system. If the system temperature is lower than the light component critical temperature the light component critical pressure is considered to be the convergence pressure. Bulk average critical temperature and bulk critical pressure of pseudo-heavy component is calculated [4].

$$T_{b.av} = \frac{\sum_{i=2}^N x'_i M_i T_{cri}}{\sum_{i=2}^N x'_i M_i} \quad (9)$$

$$P_{b.av} = \frac{\sum_{i=2}^N x'_i M_i P_{cri}}{\sum_{i=2}^N x'_i M_i} \quad (10)$$

Using the obtained data according to the diagram convergence pressure is determined and its value is compared with the preset value. They should agree within 8–12 %. If this condition is met the equilibrium constants are calculated correctly.

Almost all methods, including equation of state, which is used for calculating phase equilibrium in the multicomponent system, are based on the principle of calculating multicomponent equilibrium on the basis of binary interaction-interaction of molecules of one couple of substances which forms a system. Additional influence on the system equilibrium state, which is caused by the simultaneous interaction of molecules of three or more substances, is considered to be very insignificant comparing with the influence of binary interaction and so

it is not taken into consideration and is included in the total error. This principle is proved to be quite reliable one as the experimental results obtained using binary systems are accurate [5].

2.3. Analysis of the Basic Gas-Condensate Systems Formation Mechanisms in the Process of Inertial-Filtering Separation

As it is known, gas-condensate systems contain both solid mechanical impurities and high-dispersive drop moisture. The difference between liquid and solid disperse phases is that in the first case the particles have a smooth spherical shape and they merge in coagulation process, thus forming also individual spherical particles. Solid particles can be of various shapes, which in coagulation process form separate multi-component structures and they, in turn, also have different shapes. Imaginary density of such particles can be much less than the density of the material they are formed of.

Usually separation processes of the gas fluid mixtures take place when equilibrium air dispersed systems (their equilibrium is established in the pipeline) enter the separation channels and already formed drops are separated from gas or other admixtures in the separator.

Thus, for increasing separation efficiency and depuration of natural gases it is necessary to create the conditions when phase equilibrium breaks inside the separator, which requires analysis of the mechanisms and physical conditions of such systems formation.

When inertial-filtering separation process takes place and gas-liquid system thermodynamic parameters are changed steam condensation takes place in the gas flow. This process is possible only when the steam is saturated to the critical level [1]:

$$s_{cr} = \exp \left[1.74 \cdot 10^7 \frac{M_L}{r_L} \left(\frac{\Sigma}{T} \right)^{3/2} \right] \quad (11)$$

where M_L –condensing steam molar weight; ρ_L – liquid density.

Condensation nuclei can be little droplets. When equilibrium is established on the droplet surface Kelvin formula can be used to determine the super saturation degree [6]:

$$\ln(s) = \frac{2\Sigma M_L}{RT r_L r} \quad (12)$$

where R – gas constant; r – drop radius.

Saturated steam pressure is higher over convex surface of the drops (than that of the flat one) due to the capillary pressure and it increases when drop radius decreases [6]. Therefore, steam supersaturation is a necessary condition for steam condensation in the gas volume as it helps to compensate overpressure.

Condensation rate on the droplet surface is determined by the steam diffusion to the surface, so when supersaturation rate changes rapidly ds/dt diffusion rate can be insufficient to align steam pressure completely. In this case, steam pressure near surface of the drops can significantly differ from steam pressure in the mixture column. The result is sufficient supersaturation, leading to intense nucleation at the initial stage of the process.

Condensation is an exothermic process and much heat is released when it takes place; the temperature of the condensate drops increases, which causes heat exchange between drops and gas mixture and as a result condensation rate decreases.

When fog is formed supersaturation decreases due to steam condensation on the condensation centers. This decreasing continues till equilibrium is reached in the system, when supersaturation is equal to unit. But for effective separation of the gas-fluid system such equilibrium is not desirable. Therefore it is necessary to remove heat from the surface of the inertial-filtering separator walls, which would allow further steam condensation in the gas-fluid flow.

Liquid drops coagulation and fragmentation take place also in the gas-liquid mixture turbulent flow of pipeline or in the separation sections of inertial-filtering separator. These processes occur simultaneously till dynamic equilibrium is established in the flow. Drops in the turbulent gas flow break when their radius exceeds the critical one [1]. Drops having smaller radius than the critical one can only coagulate. Small-scale flow fluctuations cause drops deformation and breakup, since the large-scale fluctuations are changed very insignificantly at the distances like drop diameter.

Drop can not break up if dynamic pressure counteracts with surface tension force. Therefore, drop equilibrium is possible if the above quantities are equal [6]:

$$0.5 r_L^{2/3} \cdot \epsilon_0^{2/3} \cdot r^{2/3} = \frac{2\Sigma}{r} \quad (13)$$

where ϵ_0 – specific dissipation of energy.

Using Eq. (13) we can find the drop critical radius – maximal radius for drop equilibrium, if its radius is bigger than the critical one drop will break up.

$$\frac{R_{cr}}{d} = k_f^{-3/5} \cdot We^{-3/5} \cdot \left(\frac{r_G}{r_L} \right)^{2/5} \quad (14)$$

The Weber criterion We is used for determining drop stability limit.

Intensive drops coagulation is very important for liquid phase drops enlargement in the separation process. There are two basic mechanisms of drops coagulation: inertial mechanism and turbulent diffusion [1, 6]. Inertial mechanism is based on the assumption that turbulent fluctuations do not capture the drop completely. As a result relative rates acquired by drops due to turbulent fluctuations depend on drops mass. Turbulent diffusion is based on the assumption that turbulent fluctuations are strong enough to capture the drops completely and the fluctuations play an important role in drops binding. Since drops move randomly under the influence of turbulent fluctuations, their movement is similar to the diffusion phenomenon and it can be characterized by turbulent diffusion coefficient.

Inertial mechanism of coagulation. Let's consider a drop of radius r_2 . The number of this drop meetings with drops of radius r_1 per time unit under the influence of the inertial mechanism in a turbulent flow [1, 6]:

$$b_{12} = p(r_1 + r_2)^2 \cdot (r_1^2 - r_2^2) \cdot \frac{r_L \cdot e_0^{3/4}}{r_G \cdot u_G^{5/4}} \cdot n_1 \quad (15)$$

Equation of drops number n balance by the inertial mechanism [6]:

$$\frac{dn}{dt} = -\frac{1}{2} \cdot p \cdot r_{av}^4 \frac{r_L \cdot U^{9/4}}{r_G \cdot u_G^{5/4} \cdot d^{3/4}} \cdot n^2 \quad (16)$$

where r_{av} – drop average radius; U – average flow rate; ν_G – gas kinematic viscosity; ρ_G – gas density.

In the right part of Eq. (16) coefficient $\frac{1}{2}$ is used, since when calculating the number of collisions the interaction of identical drops is counted twice.

Drops volume content [6]:

$$W = \frac{4}{3} \cdot p \cdot r_{av}^3 \cdot n \quad (17)$$

Then the formula (16) will be:

$$\frac{d}{dt} \left(\frac{r_{av}}{r_{av}^0} \right) = \frac{W}{8} \cdot \left(\frac{r_{av}}{r_{av}^0} \right)^2 \cdot r_{av}^0 \cdot \frac{r_L \cdot U^{9/4}}{r_G \cdot u_G^{5/4} \cdot d^{3/4}} \quad (18)$$

where r_{av}^0 – initial radius of the drops.

Mechanism of turbulent diffusion. Let's consider two maximum possible cases $r_2 \ll r_1$ and $r_2 \sim r_1$ not taking into consideration the surrounding resistance.

In the first case, drops get close under the influence of fluctuations $\lambda \sim R - R_1$ and in the second – $\lambda \sim R$, where R – distance between the centers of considered drops. Using these limiting correlations as well as the symmetry condition $\lambda(R, r_1, r_2) = \lambda(R, r_2, r_1)$ we obtain the following formula for determination of the fluctuations which can bring together drops of arbitrary radius [6]:

$$I \sim R - r_1 - r_2 + \frac{r_1 \cdot r_2 \cdot (r_1 + r_2)}{r_1^2 + r_2^2 - r_1 \cdot r_2} \quad (19)$$

Turbulent diffusion coefficient without motion limitation of the drops [6]:

$$D = \frac{m_G}{r_G \cdot I^2} \cdot I^2 \quad (20)$$

3. Conclusions

Having analyzed thermodynamic characteristics of the gas-condensate mixtures and determined the conditions of their phase equilibrium one can make a conclusion that moisture in the form of liquid drops which enters the separation channels is the necessary condition for effective gas-fluid mixtures separation in the inertial-filtering gas separator.

Therefore, a special processes causing supersaturation of the mixture should take place to achieve the effective separation in the gas flow. It is very important to know the best values and correctly regulate thermodynamical parameters of the system to intensify the mechanisms of formation or enlargement of the drops in the gas-fluid flow in inertial-filtering separation.

Based on the analysis of the best thermodynamic separation modes it is proposed to fulfill separation inside the gas separator, in other words, to use this method in new alternative constructions of separator-condensers, where both processes separation and condensation take place simultaneously within one device.

Using such separators one can fulfill effective separation of gas-fluid systems having considerable quantity of steam-like moisture and also remove coarse fractions of hydrocarbon from gas (gasoline extraction from gas).

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АНАЛІЗ УМОВ ФАЗОВОЇ РІВНОВАГИ І ВПЛИВУ СПОЛУЧЕНОГО ТЕПЛОМАСООБМІНУ НА ЕФЕКТИВНІСТЬ ПРОЦЕСУ РОЗДІЛЕННЯ В ІНЕРЦІЙНО- ФІЛЬТРУЮЧОМУ СЕПАРАТОРІ

Анотація. Розглянуто основні термодинамічні параметри, які мають найбільший вплив на ефективність протікання процесів розділення газорідинних сумішей, а також на фазову рівновагу таких систем. Дано загальна характеристика процесів сепарації з урахуванням фазової рівноваги. Проаналізовано основні підходи до розрахунку фазової рівноваги і сполучного теплообміну. Виявлено можливі шляхи удосконалення та розвитку газосепараційної техніки.

Ключові слова: моделювання, рівновага, газорідинна суміш, критичні параметри, константа фазової рівноваги, термодинамічні параметри, конденсація.