

Analysis of the Phase Equilibrium Conditions and the Impact of Coupled Heat and Mass Transfer on the Separation Process Efficiency in the Inertial – Filtering Gas Separator

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Abstract – This article deals with the basic thermodynamic parameters which have the greatest impact on the efficiency of the gas-liquid mixtures separation processes and on the phase equilibrium of such systems. One gives general characteristic of the separation processes, taking into account phase equilibrium. The basic approaches to the calculation of phase equilibrium and coupled heat transfer are analyzed in this paper. Possible ways of gas separation devices improvement and development are described.

Key words – modeling, equilibrium, gas-liquid mixture, critical parameters, phase equilibrium constant, system thermodynamic parameters, equation of state, condensation, coagulation.

I. Introduction

Extracted from the depths of the oil fields hydrocarbon gases are saturated with water vapor. Raw natural gas includes large amount of liquid drops, consisting of mineralized water and gas condensate, as a rule, in the amount of 30-40 g/m³, and sometimes 200-800 g/m³. Therefore, such gas condensate mixtures before they enter the main pipelines or productions lines are subjected to separation which includes separating mechanical impurities, water and hydrocarbon condensate.

Description and determining phase equilibrium conditions of gas condensate systems is very important when modeling gas-liquid mixtures separation processes

In case of infinite steam mass if the system has phase transitions and the initial gas temperature is lower than the droplet surface temperature, there is no limit equilibrium state because droplet size will increase endlessly due to condensation process. If gas initial temperature is higher than drops surface temperature, drop evaporates completely gas temperature becomes uniform. But if there is some finite steam mass, limit equilibrium always exists. It is determined by the initial state, solving the equations of mass and energy conservation, phase equilibrium and equation of state.

II. Analysis of the basic thermodynamic parameters affecting the gas-liquid system

Gas escape of hydrocarbon fractions C₃₊ higher chemical composition from natural and accompanying

petroleum gas (topping) is usually effected at the low temperature condensation and separation units (STC) as well as 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 occur due to internal gas energy[1].

When gas-liquid mixtures pass through these devices pipeline phase equilibrium is broken. So drops nucleation take place as a result of coupled inter phase 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 when liquid droplets enlargement take 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 chemical composition have excellent critical parameters (in particular, critical temperature and pressure), so when thermodynamic characteristics of the system are changed (and particularly when pressure grows and temperature goes down), separate components can be condensed. It has positive impact on the effectiveness of inertial-filtering separation [2].

By lowering the system temperature steam pressure of saturated components goes down and the system becomes inequilibrium and some part of components transfer to the liquid phase in the form of mono dispersed drops; which means partial condensation takes place in the gas liquid mixture. To reach condensation of separate gas liquid mixture component its partial pressure must correspond to the steam pressure at a given temperature. So 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 – mol fraction of the i component in the gas phase;

x_i – mol fraction of the i component in the liquid phase.

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

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

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

where V – mol fraction of gas phase in the mixture;

L – mol fraction of the liquid phase in the mixture;

z_i – mol fraction of the i component in the mixture.

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

Gas and liquid phases fugacity coefficients:

$$\varphi^G = \frac{f_i^G}{P \cdot y_i} \quad (4)$$

$$\varphi^L = \frac{f_i^L}{P \cdot x_i} \quad (5)$$

where f_i^G и f_i^L – fugacity of gas and liquid phases, respectively.

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

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

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

$$K_i = \frac{\varphi^L}{\varphi^G} \quad (7)$$

III. Analysis of the main phase equilibrium calculation 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 ideal gas. This is particularly noticeable at low temperatures and high pressures. Therefore, there are many equations of state to determine and describe the properties of hydrocarbon systems. Among the most widely used equations of state one can call the equation Redlich – Kwong, modified by Souv, Peng – Robinson equation, Benedict – Webb – Rubin equation, modified by Starling. Each equation of state has its advantages and disadvantages. The solution of these equations is performed by 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 equations (2 – 3).

Graphical methods are very accurate for manual calculations of phase equilibrium constants. The most simple and accurate one is NGPA method[3].

Using this method the 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, the vertical axis – phase equilibrium constant of a particular system component (pic. 1.1 shows one of such graphics for methane convergence pressure 800psi). In these coordinates there are isotherms which converge at $K = 1$, and at pressure equal to the system convergence pressure. For different mixtures with the same pressure convergence equilibrium constants of the identical components have the same meanings at equal pressures and temperatures.

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

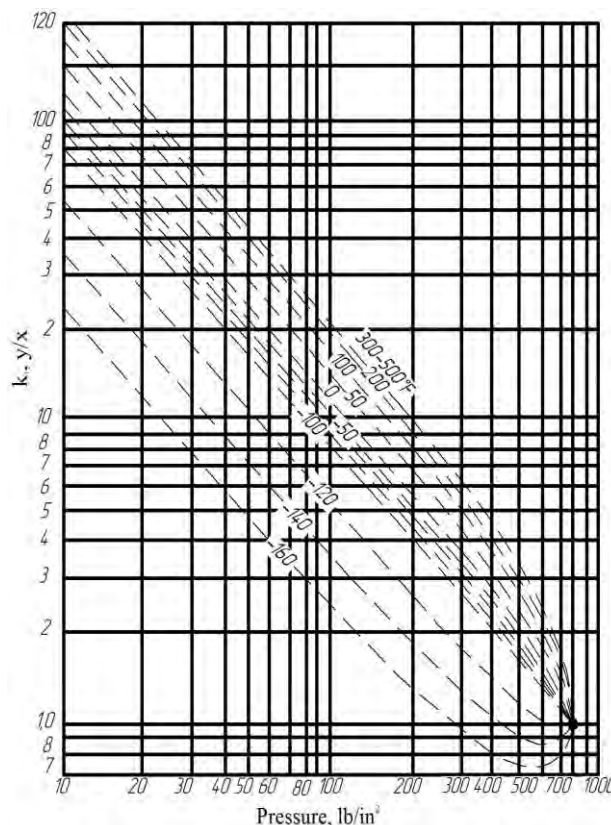


Fig. 1. Equilibrium constants graphic for methane
 $P_{cx} = 800$ psi

Using the obtained phase equilibrium constants, equilibrium composition of the 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 – mol fraction of the steam phase.

Convergence pressure is determined by Hadden method [3]. 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 the 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. One calculates bulk average critical temperature and bulk critical pressure of pseudo-heavy component:

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

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

Using the obtained data according to the graphic one determines convergence pressure which value is compared with a preset. They should agree within 8-12%. If this condition is met, the equilibrium constants are defined correctly.

IV. Analysis of the basic gas-condensate systems formation mechanisms when using inertia-filtering separation

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

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

$$s_{cr} = \exp \left[1,74 \cdot 10^7 \frac{M_L}{\rho_L} \left(\frac{\Sigma}{T} \right)^{3/2} \right] \quad (11)$$

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

Condensation nuclei can be little droplets, wherein when equilibrium is established on the droplet surface, Kelvin formula can be used to determine the super saturation degree[4]:

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

where R – gas constant;
 r – drop radius

Saturated vapor pressure is higher over drops convex surface (than that of the flat one) due to the capillary pressure and it increases when droplet radius decreases [4]. Therefore, steam supersaturation is a necessary condition for vapor condensation in the gas volume as it compensates over- pressure.

Fig. 1.2 shows the supersaturation dependence on time. Condensation rate on the droplet surface is determined by the vapor diffusion to the surface, so when supersaturation rate change is high ds / dt diffusion rate can be insufficient to align steam pressure in the entire volume. In this case, steam pressure on the droplets surface can significantly differ from steam pressure in the mixture column. The result is high supersaturation, resulting intense nucleation at the initial stage of the process.

Liquid droplets coagulation and fragmentation takes place also in the gas-liquid mixture turbulent flow of pipeline or separation sections of inertial – filtering separator. These processes occur simultaneously, till dynamic equilibrium is established in the flow. Drops in the turbulent gas flow are broken when their radius exceeds some critical radius [1].

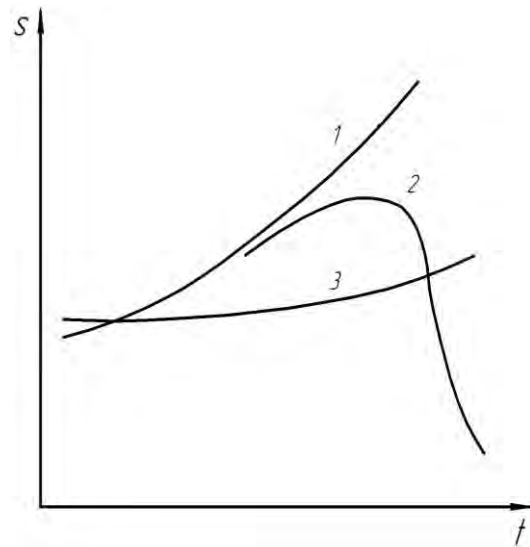


Fig. 1.2 Vapor supersaturation dependence on time: 1, 2 -, without considering/considering liquid phase nucleation respectively, 3 – critical supersaturation

Drops of the size less than the critical radius can only coagulate. Small-scale flow fluctuations cause drops deformation and breakup, since the large-scale fluctuations changes are very insignificant at the distances like drop diameter.

If dynamic pressure counteracts with surface tension force drop can not break up. Therefore, drop equilibrium is possible if above quantities are equal. [4]:

$$0,5 \rho_L^{2/3} \cdot \varepsilon_0^{2/3} \cdot r^{2/3} = \frac{2\Sigma}{r} \quad (13)$$

where ε_0 – energy specific dissipation.

Using equation (13) we can find the drop critical radius, ie, maximum radius for drop equilibrium, if drops radius is bigger than the critical one the drop will break up.

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

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, 4]. Inertial mechanism is based on the assumption that turbulent pulsations don't capture the drop completely. As a result relative speeds acquired by drops due to turbulent fluctuations depend on droplets 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 drop move randomly under the influence of turbulent fluctuations, their movement is similar to the diffusion phenomenon and 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, 4]:

$$\beta_{12} = \pi (r_1 + r_2)^2 \cdot (r_1^2 - r_2^2) \cdot \frac{\rho_L \cdot \varepsilon_0^{3/4}}{\rho_G \cdot v_G^{5/4}} \cdot n_1 \quad (15)$$

Where $n_1 - r_1$ radius droplets number in unit volume.

Drops number balance equation – n , due to the inertial mechanism:

$$\frac{dn}{dt} = -\frac{1}{2} \cdot \pi \cdot r_{av}^4 \cdot \frac{\rho_L \cdot U^{9/4}}{\rho_G \cdot \nu_G^{5/4} \cdot d^{3/4}} \cdot n^2 \quad (16)$$

where r_{av} – drop average radius;

U – mean flow rate;

ν_G – gas kinematic viscosity;

ρ_G – gas density.

In the right part of the formula (16) there is a coefficient 1/2, as when calculating the number of collisions the interaction of identical drops is counted twice.

Droplets volume content:

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

Then the formula (16) will be:

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

Where r_{cp}^0 - the initial radius of droplets.

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

In the first case, drops get close under the influence of pulsations $\lambda \sim R - R_1$, and in the second – $\lambda \sim R$, where R – the 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 estimation of the pulsations which can bring together drops of arbitrary radius [4]:

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

Turbulent diffusion coefficient without motion limitation of the drops:

$$D = \frac{\mu_G}{\rho_G \cdot \lambda_0^2} \cdot \lambda^2 \quad (20)$$

Conclusion

No doubt, drop liquid which enters into the separation channels of the inertial-filtering gas separator is the necessary condition for effective gas liquid mixtures

separation. To achieve the effective separation in the gas flow special processes causing mixture supersaturation must take place. It is very important to know the best values and correctly regulate system thermo dynamical parameters using additional devices at the PCU inlet or within the gas separator, as by new unique separators-condensators [5], where both processes separation and condensation take place simultaneously within one device.

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