Modelling of mass transfer in separation of hydrocarbon mixtures and modernization of industrial columns

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Abstract. A system of differential equations of mass transfer with an interfacial mass source for multicomponent distillation in a column with random and structured packings in the film mode is presented. The interfacial source is associated with the matrix of volumetric mass transfer coefficients as well as a driving force for mass transfer. The diffusion fluxes of mass of components are written in the form of Fick’s law with elements of the matrix of coefficients of molecular diffusion in the gas (vapor) phase. To simplify the mathematical model, one-dimensional equations for the diffusion model of the structure of flows in the gas and liquid phases with the interfacial sources and coefficients of back (longitudinal) mixing of gas and liquid flows are used. The Dankwerts boundary conditions are applied to the system of equations. To calculate the back mixing coefficients, experimental data obtained for the selected types of packings are used. When modelling mass transfer in hydrocarbon mixtures consisting of several dozen components, the system of equations for the diffusion models is solved for the key components and fractions of the oil and gas condensate (OGC) mixture stabilization column at an industrial enterprise. A brief description of the technological scheme is given. Scientific and technical solutions are developed to replace obsolete sieve trays in the stabilizer column with a new structured corrugated roll packing having a rough surface. It is found that a packing height of eight meters is sufficient for separating OGC in a given composition range. As a result of implementation of the new packing, the content of isopentane in the stable condensate decreases and its concentration in the broad fraction of light hydrocarbons increases from 9 wt.% to 11.7 wt.% . The implementation of packing in the stabilizer column meets the requirements of the technical specifications.

1. Introduction

The problem of modelling the separation of multicomponent mixtures (MCM) into whole components is important and relevant for both fundamental and applied science in various industries [1]. To solve this problem, various approaches are used in chemical engineering [2-4] with the introduction of various types of contact devices [5-7], mainly bubble trays, structured and random packings [5; 8-10].

When modelling processes in multicomponent mixtures, it is necessary to take into account the influence of the main and cross effects, as well as, in some cases, heat transfer between phases. In this regard, the mathematical description of mass transfer processes is a complex problem, in the solution of which it is necessary to use matrix equations.
2. Mathematical model

The purpose of the present work is mathematical modelling of the separation of a multicomponent mixture (MCM) in a column for stabilizing oil and gas condensate.

In the numerical modelling of transfer of momentum, mass of components and heat in film devices with a random packing, a system of partial differential equations for the continuous phase, i.e. gas (vapor), is written and the interaction with a falling liquid film on the surface of random elements is taken into account using volumetric interfacial sources. The sources depend on characteristics of the boundary layer at the interface and the driving forces of the process [7-8]. For example, with a known profile of gas velocity in the cross-section of the packed column, the equations of mass transfer in the MCM in a cylindrical coordinate system have the form:

\[
\frac{\partial c_{gi}}{\partial z} + \text{div}_{j} = \sum_{i=1}^{n-1} \left( (K_{vgij} a) (c_{gi}^* - c_{gi}) \right)
\]

(1)

where \(c_{gi}\) is concentration of the \(i^{th}\) component in the gas phase; \(w_g(r)\) is gas velocity as a function of the radial coordinate, m; \(Z\) is vertical coordinate, m; \((K_{vgij} a)\) are elements of the matrix of volumetric mass transfer coefficients, \(s^{-1}\); \(c_{gi}^*\) is equilibrium concentration; \(n\) is number of components in the mixture; \(j\) is mass flux density.

Equation (1) is supplemented by the expression for the mass balance of components through the interface and the conditions of thermodynamic equilibrium.

Diffusion fluxes of components are written in the form of Fick’s law, taking into account the molecular turbulent transfer:

\[
\frac{\partial c_{ig}}{\partial r} = \rho_g \sum_{i=1}^{n-1} (D_{ij} + \delta_{ij} D_T) \frac{\partial c_i}{\partial r}
\]

(2)

\[
\frac{\partial c_{ig}}{\partial z} = \rho_g \sum_{i=1}^{n-1} (D_{ij} + \delta_{ij} D_T) \frac{\partial c_i}{\partial z}
\]

(3)

where \(D_{ij}\) is element of the square matrix of molecular diffusion coefficients \([D]\) with dimension \((n-1)(n-1)\); \(D_T\) is turbulent diffusion coefficient, \(m^2/s\); \(\delta_{ij}\) is Kronecker’s delta; \(\rho_g\) is gas density, \(kg/m^3\); \(n\) is number of components.

To simplify the presented mathematical model, the flow structure models can be used [7-8].

The most widely used for calculating the concentration profiles of components in packed columns is the diffusion model of the flow structure, which takes into account the back mixing of gas and liquid flows. In the equations considered below, it is assumed that the interphase transfer is determined by equimolar mass transfer, which leads to the constancy of mass fluxes of vapor and liquid along the column height during distillation.

The levels of one-dimensional steady-state diffusion models written for the gas (vapor) and liquid phases have the form molecular turbulent transfer:

\[
\frac{d c_{gi}}{d z} = \sum_{i=1}^{n-1} \left( (K_{vgij} a) (c_{gi}^* - c_{gi}) \right) + \frac{d c_{eq}}{d z} \frac{d^2 c_{gi}}{d z^2},
\]

(4)
\[
\frac{dc_{li}}{dz} = S \sum_{i=1}^{n-1} (K_{vgi})(c_{gi}^{*} - c_{gi}) - \frac{d_{eq}}{Pe_{l}} \frac{d^2 c_{li}}{dz^2},
\]

(5)

where \(L, G\) are mass flowrates of liquid and gas, respectively, kg/s; \(S\) is cross-sectional area of the column, m\(^2\); \(d_{eq}\) is equivalent diameter of the packing, m; \(Pe_{g}, Pe_{l}\) are Peclet numbers (criteria) for back mixing in the gas and liquid phases, respectively; \(Pe_{g} = \frac{w_g d_{eq}}{D_{mg}}\); \(Pe_{l} = \frac{u_l d_{eq}}{D_{ml}}\); \(w_g, u_l\) are average gas and liquid velocities, respectively, m/s; \(D_{mg}, D_{ml}\) are coefficients of back mixing of flows, m\(^2\)/s.

The Dankwerts boundary conditions are applied to equations (4), (5):

- at \(z = 0\) (gas inlet and liquid outlet):

\[
c_{gi} = c_{gsi} - \frac{dc_{gi}}{Pe_{g} dz}; \quad \frac{dc_{li}}{dz} = 0,
\]

(6)

- at \(z = H\) (gas outlet and liquid inlet):

\[
c_{li} = c_{lsi} + \frac{dc_{li}}{Pe_{l} dz}; \quad \frac{dc_{gi}}{dz} = 0,
\]

(7)

where \(H\) is height of the packed bed, m; indices: \(s\) are initial (starting) values of concentration.

To calculate Peclet numbers, generalizations of experimental data for each type of packing are used. In the gas phase, expressions derived from the Taylor model [8] can be applied.

An expression for determining the matrix of mass transfer coefficients follows from the additivity equation of phase resistances:

\[
[K_{vg}] = [m][\beta_{l}]^{-1} + [\beta_{g}]^{-1},
\]

(8)

where \([m]\) is matrix of distribution (equilibrium) coefficients; \([\beta_{l}], [\beta_{g}]\) are matrices of mass transfer coefficients in the liquid and gas phases, respectively, which are determined in accordance with the mathematical model of the boundary layer [8].

3. Distillation column modernization

An example of modernization of an oil and gas condensate (OGC) mixture stabilization column at an oil refinery is considered.

The stabilizer column has a variable cross-section (the upper part is smaller than the lower one) with 38 multi-pass sieve trays. In the upper part there are 19 four-pass trays with a diameter of 2.6 m, and in the lower part there are 19 six-pass trays with a diameter of 3.2 m. The load interval for the oil and gas condensate mixture is from 160 to 250 m\(^3\)/h. The distillation process in the column takes place at a pressure of 0.6-1.4 MPa and temperatures: column bottom - no more than 250 °C; column top - no more than 150 °C.

The heated OGC mixture is fed to the central part of the column. In the upper part of the column, vapors of a broad fraction of light hydrocarbons (BFLH) are removed, where they are further condensed in a refrigerator-reflux condenser and enter the reflux tank. Part of the BFLH from the tank is fed for further processing or storage, while the other part goes back to the column in the form of cold reflux. Stable condensate (up to 250 °C) is removed from the stabilizer bottom through a heat exchanger-recuperator for heating the initial mixture. Part of the bottom mixture is heated in the furnace and returned to the column in the form of a "hot stream".
Based on the use of a mathematical model, calculations are performed and an analysis of the stabilizer column operation is made. It is found that the change in the composition of \( \text{C}_6 \) and higher in the initial mixture from 65 wt. % to 49 wt. % leads to a decrease in the maximum productivity from 550 to 410 m\(^3\)/h due to insufficient throughput of the trays in the upper part of the column. Replacement of sieve trays in the upper part of the column with structured roll packing “Inzhekhim” having a corrugated surface and roughness is considered. The packing is made of metal strips and, depending on the corrugation height, can have a specific surface area of 200 to 350 m\(^2\)/m\(^3\).

To operate at increased loads, calculations are made for the packing with \( \alpha = 200 \text{ m}^2/\text{m}^3 \) [8]. The task of the calculation is to determine the height of the packing for the given operating and design characteristics and the quality of mixture separation. The input concentrations of the components and the flow rate of the mixture into the packed section are determined from the tray-by-tray calculation by the method of theoretical trays and the results are compared versus the data of the industrial operation of the column.

However, modelling of mass transfer in a mixture consisting of several dozen components is laborious; therefore, the calculation is performed for the following key components: propane, isobutane, n-butane, isopentane and a fraction of 40-50 °C.

As a result of calculations, it is found that the height of the packed bed \( H = 8.0 \text{ m} \) is sufficient for a given quality of the mixture separation when operating with an increased load up to 550 m\(^3\)/h, and for the feedstock load of the OGC mixture - up to 250 m\(^3\)/h. As a result of the introduction of structured packing, the content of isopentane in the stable condensate is reduced. The data of industrial operation of the column after the introduction of packing show that the content of isopentane in BFLH increases from 9-10 wt. % to 11.7 wt. % and the content of the \( \sum \text{C}_6 \) components decreases to 0.36 %.

4. Conclusion
This article shows an example of mathematical modelling of a multicomponent hydrocarbon mixture based on the use of flow structure models and the introduction of a new roll packing in a stabilizer column of an oil and gas condensate mixture. The calculation is carried out for the key components and the required packed bed height is selected to provide the specified amount of mixture separation.

The developed mathematical model and the considered roll packing can be used to solve scientific and technical problems of designing new columns or modernizing existing ones at oil and gas refining enterprises.

Acknowledgments
The study was carried out within the framework of the scientific project of the Russian Science Foundation No. 18-79-101-36.

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