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RESEARCH ARTICLE

Analysis of the rectifying separation of H_2O–D_2O mixture into light and heavy water by means of mathematical modeling

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Abstract

Objectives. *To apply an analytical method for the calculation of a distillation column for the production of D_2O at a two-column Kuhn installation operating under vacuum: to simulate the Kuhn installation in the Hysys software; and to compare experimental and calculated data.*
Methods. *Analytical method for the calculation of distillation columns "from stage to stage," from the lower theoretical separation stage (TSS) to the upper stage. This method is based on phase equilibrium at the TSS with known data of input flows and component concentrations in the column bottoms. Hysys was used as modeling software.*
Results. *Comparison of the calculation results with Kuhn's experimental data testified to the high calculation accuracy of the vapor–liquid phase equilibrium for the H_2O–D_2O mixture at the TSS. The convergence of the D_2O material balance for the entire installation was 0.005%. The identification parameter was the number of the column feed plate. Simulation of the Kuhn installation in the Hysys software showed a qualitative agreement of D_2O concentrations in material flows. The UNIQUAC (UNIversal QUAsiChemical) model was used to calculate activity coefficients. The found values of the number of theoretical separation stages (NTSS) in both columns, were 88 and 153 taking into account the reboiler and condenser. This is less than the experimental 295 and 400, respectively. The discrepancy can be explained by the increased phase equilibrium H_2O constant in the UNIQUAC model. However, the convergence of the material balance in terms of D_2O was high and amounted to $1.38 \cdot 10^{-6}$%. The absolute error of the found concentrations in material flows did not exceed 0.12 mol %.*
Conclusions. *The results obtained indicated the possible use of the Hysys modeling software when searching for and optimizing the operating mode of the block diagram of a cascade of distillation columns with direct and recycle flows to separate a mixture of water into light and*

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heavy water. The final results obtained with regard to the operating mode, inlet and outlet material flows (flow rate, composition, temperature, and pressure drop across the column) are recommended for use in the analytical program for the calculation of the distillation column to refine the NTSS and distribution profile of the concentrations of the H_2O and D_2O components along the height of the column.

Keywords: *light water, heavy water, Hysys, continuous distillation, separation factor, activity coefficients of H_2O and D_2O*

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НАУЧНАЯ СТАТЬЯ

Анализ ректификационного разделения смеси H_2O–D_2O на легкую и тяжелую воду методом математического моделирования

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Аннотация

Цели. *Применение аналитического метода расчета ректификационной колонны для получения D_2O в двухколонной установке Куна, работающей под вакуумом. Моделирование установки Куна в программной среде Hysys. Сравнение экспериментальных и расчетных данных.*
Методы. *Аналитический метод расчета ректификационной колонны «от ступени к ступени» от нижней теоретической ступени разделения (ТСР) к верхней, основанный на фазовом равновесии на ТСР при известных исходных данных входных потоков и концентраций компонентов в кубе колонны. Среда моделирования Hysys.*
Результаты. *Сравнение результатов расчета с экспериментальными данными Куна свидетельствовало о высокой точности расчета равновесия фаз пар – жидкость для смеси H_2O–D_2O на ТСР. Сходимость материального баланса по D_2O по установке в целом составила 0.005%. Параметром идентификации являлся номер тарелки питания колонны. Моделирование установки Куна в среде Hysys показало качественное согласование концентраций D_2O в материальных потоках. Для расчета коэффициентов активности использована модель UNIversal QUAsiChemical (UNIQUAC). Найденные значения числа теоретических ступеней разделения (ЧТСР) в обеих колоннах с учетом ребойлера и конденсатора составляют 88 и 153, что меньше экспериментальных 295 и 400 соответственно. Расхождение объясняется повышенным значением константы фазового равновесия H_2O модели UNIQUAC, однако сходимость материального баланса по D_2O высокая и составляет $1.38 \cdot 10^{-6}$%. Абсолютная погрешность найденных значений концентраций в материальных потоках не превышает 0.12 мол. %.*
Выводы. *Полученные результаты свидетельствуют о возможном применении среды моделирования Hysys для поиска и оптимизации режима работы структурной схемы каскада ректификационных колонн с прямыми и рецикловыми потоками для разделения смеси воды*

на легкую и тяжелую воду. Полученные конечные результаты по режиму работы, входным и выходным материальным потокам (расход, состав, температура, перепад давлений по колонне) рекомендовано использовать в аналитической программе расчета ректификационной колонны для уточнения ЧТСР и профиля распределения концентраций компонентов H_2O *и* D_2O *по высоте колонны.*

Ключевые слова: *легкая вода, тяжелая вода, Hysys, непрерывная ректификация, коэффициент разделения, коэффициенты активности* H_2O *и* D_2O

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INTRODUCTION

It is impossible to improve and optimize technological schemes for the separation of homogeneous mixtures by the method of rectification without the use of modern software for modeling complex chemical-technological systems (CCTS). For this purpose, modern software is equipped with a library of component properties, modules for calculating apparatuses, mathematical modules for ensuring the convergence of calculations, equations for calculating the properties of a multicomponent mixture, etc. The availability of programming tools and the level of development of visualization allows such software as Matlab (Matrix Laboratory) to be created. This tool is a package of applied programs for technical calculations, engineering, and scientific problems in any industry. SPSS Statistics (Statistical Package for the Social Sciences) is a computer program for applied research and statistical data processing. ChemCad (Chemical Computer-Aided Design) is used mainly in modeling processes and flowsheets of chemical and petrochemical industries. Ansys Fluent is a software and computational complex for modeling the flows of liquids and gasses in the aerospace industry, automotive, turbomachinery, oil and gas, and chemical industries. Hysys (Aspen Hysys) is a programming software for technological schemes of an arbitrary structure of chemical and technological industries and other software packages for computer simulation.

Simulation of CCTS allows the results obtained to be analyzed not on an operational plant, but in computer systems with a range of different devices and technological modes of their operation. This optimizes the technological scheme allowing the desired product quality to be achieved or energy costs minimized with subsequent implementation in industrial production.

The widespread use of Hysys in CCTS modeling is due to the multi-circuit architecture in Hysys which allows an arbitrary number of circuits to be created within one calculation. If necessary, you can use your own thermodynamic package of properties in each subcircuit. A large scheme can be divided into separate sections and the mode of operation of a particular section of the technological scheme can be found. Therefore, the structure of the technological scheme, consisting of a set of apparatuses and devices, changing the parameters of their operation mode, such as process temperature, pressure, and component composition can be optimized.

In [1], the designs of heat pumps of closed and open “pipe in pipe” types were considered, while the adequacy of the computer model of the “rectification unit–heat pump of closed type” system was checked using the Hysys simulation software. In [2], the Hysys software was used to perform a simulation of a crude oil distillation unit. This included four main stages: preliminary evaporation, atmospheric, stabilizing, and vacuum.

When water is separated by distillation into light (H_2O) and heavy (D_2O) water, the number of theoretical separation stages (NTSS) is very large. Therefore, a cascade of several columns of tray or packed type is used rather than one distillation column [3]. The Hysys data library contains the physicochemical properties of the H_2O and D_2O components. In this case, the use of modern modeling software for the analysis and improvement of such

CCTS is reasonable and necessary. However, there are no publications on the study of the use of the Hysys simulation software for the separation of a mixture of H_2O–D_2O into light and heavy water.

In this paper, we propose the use of Hysys simulation software for the development of technological schemes consisting of a cascade of distillation columns with direct and recycle flows to separate the H_2O–D_2O mixture into light and heavy water. This is followed by refinement of the NTSS and the profile of the distribution of component concentrations along the height of the column based on the analytical column calculation method [4].

METHODS

The modeling of distillation is based on the calculation of the vapor–liquid phase equilibrium at the theoretical separation stage (TSS), the reliability of the description of which affects the quality of the separated products. The main difficulty is the choice of an equation for calculating the activity coefficients of the components.

The group composition models the following: UNIversal Functional Activity Coefficient (UNIFAC), UNIversal QUAsiChemical (UNIQUAC), Non Random Two Liquid (NRTL) models, etc. It also models their modifications [5], which have proven themselves well in the calculation of column distillation apparatuses in the chemical industry. Such have been widely developed in chemical [6], oil refining, petrochemical [7], and alcohol industries [8, 9] in the separation of multicomponent mixtures with a slight deviation from the Raoult law and azeotropic mixtures in the production of bioethanol [10, 11], characterized by strong nonideality.

In the analytical methods proposed for calculating column apparatus when separating a mixture of H_2O–D_2O into light and heavy water, the activity coefficients γ_{H_2O} and γ_{D_2O} were not considered [3], or the mixture was classified as ideal both in the liquid and vapor phases [12]. It is equivalent to equating the activity coefficients to units.

We have shown [4] that the H_2O–D_2O mixture is not ideal, i.e., it does not obey the Raoult law. Based on the material balance equations, the equilibrium equation, and the equation for calculating the separation coefficient (H.C. Urey), Eqs. (1) and (2) for calculating the activity coefficients of the H_2O and D_2O components were obtained based on the assumption that the mixture being separated consists of two components H_2O and D_2O. A method for the calculation of the column “from stage to stage,” including the calculation of phase equilibrium on the TSS, was proposed.

$$\gamma_{H_2O} = \frac{1}{\frac{P^{\circ}_{H_2O}}{P} x_{H_2O} + \alpha_{H-D} \frac{P^{\circ}_{D_2O}}{P} x_{D_2O}}, \tag{1}$$

$$\gamma_{D_2O} = \frac{1}{\frac{1}{\alpha_{H-D}} \frac{P^{\circ}_{H_2O}}{P} x_{H_2O} + \frac{P^{\circ}_{D_2O}}{P} x_{D_2O}}, \tag{2}$$

The activity coefficients of the H_2O and D_2O components are interconnected by the separation factor α_{H-D}.

$$\gamma_{D_2O} = \alpha_{H-D} \cdot \gamma_{H_2O} \tag{3}$$

Based on a comparison of experimental and calculated data, the applicability of this method to the separation of an isotopic mixture of H_2O–D_2O into light and heavy water is shown.

RESULTS AND DISCUSSION

Let us apply the method of calculating a distillation column for separating a mixture of H_2O–D_2O, as described in [4], to the well-known experimental two-column Kuhn installation for obtaining D_2O. The material balance of this installation is shown in Fig. 1 [13]. The height of the separating part of the first stage is 530 cm; the height of the equivalent theoretical stage (HETS) is 1.8 cm; the height of the separating part of the second stage is 680 cm; while HETS is 1.7 cm. The pressure in the upper part of the first stage is 120 mm Hg, and the pressure in the upper part of the second stage is 60 mm Hg. The calculation will be carried out for each stage separately. In relation to the hardly volatile component D_2O, the input flow (feed) divides the column into two parts: the upper (exhaustive) and the lower (strengthening). By analyzing the initial data of the Kuhn installation (Fig. 1), we can determine the values of the quantities necessary for modeling each stage (Tables 1 and 2). In Fig. 1 and in Tables 1 and 2, the concentration of D_2O is given in mol %.

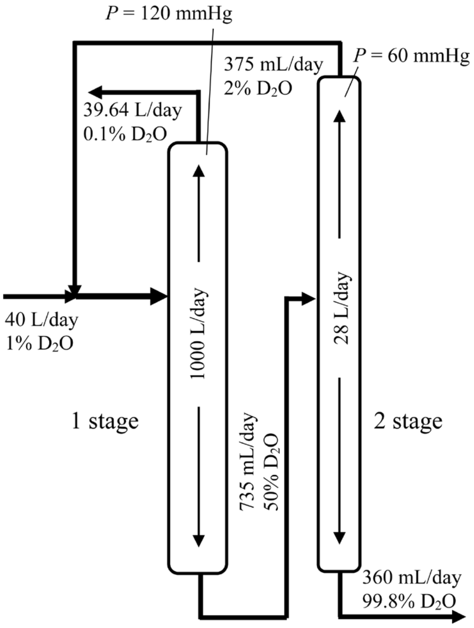


Fig. 1. Scheme of material balance of two-stage Kuhn plant to obtain D_2O.

In Tables 1 and 2, the reflux ratio R is defined as the ratio of the amount of liquid stream flowing down the column, to the amount of distillate withdrawn from the top of the column. The molar flow rates of material flows are determined by known expressions. These expressions take into account the average value of the density and the average value of the molar mass of the flow, depending on the concentrations of the H_2O and D_2O components in the flow. When recalculating, the following is assumed: the molar mass of H_2O is 18.02 kg/kmol, D_2O is 20.03 kg/kmol; while the density, taking into account the separation process under vacuum H_2O, is 998 kg/m^3, D_2O 1108 kg/m^3 [14, 15]. NTSS in columns is determined by the ratio of the height of the separating part of the stage to HETS. In the first approximation, it is assumed when modeling that the pressure at the bottom of the first stage is 18 kPa, the pressure of the second stage is 9 kPa.

The feed plate number was taken as the identification parameter. The calculation of the column was carried out by the method "from stage to stage" from the bottom up. The plates are numbered from bottom to top. The results of the calculation are shown in Fig. 2. The convergence of the material

Table 1. Initial data of the Kuhn installation

Stage number	Material flows							
	L/day				kmol/day			
	F	D	W	Rec	F	D	W	Rec
1 stage	40	39.64	0.735	0.375	2.20202	2.18216	0.0405	0.02064
2 stage	0.735	0.375	0.36	–	0.0405	0.02064	0.01986	–

Note: F is feed; D is distillate; W is bottom residue; Rec is recycling.

Table 2. Initial data of the Kuhn installation (continued)

Stage number	D_2O concentration, mol %				P, kPa	R	f	NTSS
	x_F	x_D	x_W	x_{rec}				
1 stage	1.0	0.1	50	2.0	16	25.227	1.0091	295
2 stage	50	2.0	99.8	–	8	74.667	1.9622	400

Note: x_F, x_D, x_W, x_{rec} are D_2O concentrations in feed, distillate, bottoms, and recycle, respectively; P is the pressure of the top of the column; R is the reflux ratio; $f = F/D$.

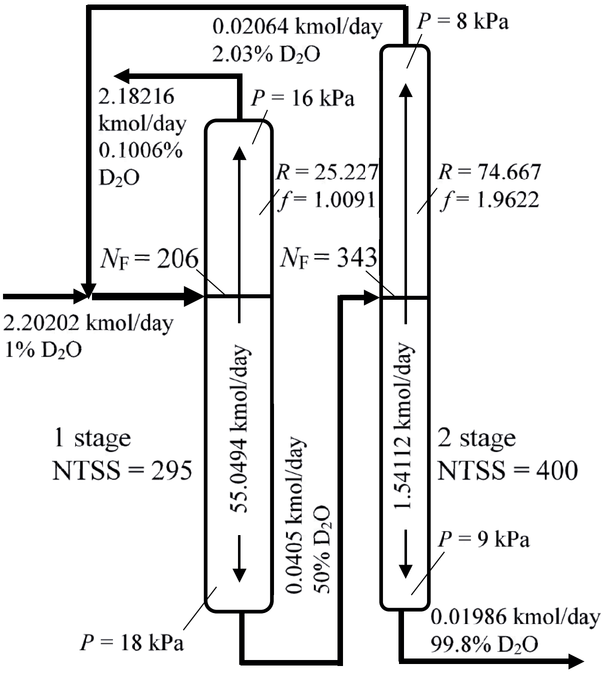


Fig. 2. Calculated data for the two-column Kuhn installation based on the analytical calculation method.

balance for D_2O for the entire plant was 0.0005%. The profile of the change in D_2O concentration along the height of the columns at the first and second stages is shown in Fig. 3.

Point *a* characterizes the transition from the strengthening part of the column to the exhaustive part. The observed break in the curves of the concentration profile corresponds to the general ideas regarding the change in concentrations in the liquid phase in the feed zone of the distillation column.

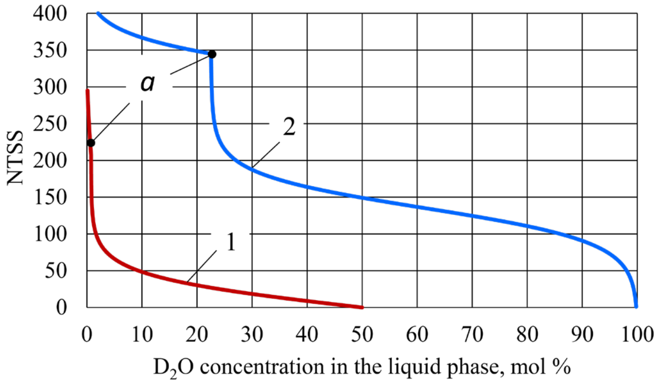


Fig. 3. Profile of change in the D_2O concentration along the height of the columns based on the analytical method of calculation: (1) first stage; (2) second stage.

Analysis of the dependence of the activity coefficient of the H_2O and D_2O components on the mixture composition at $P = const$

Based on the algorithm for calculating the boiling point of a mixture of H_2O–D_2O, as described in [4], incorporating a block for calculating phase equilibrium on TSS, a program was developed in the Borland Pascal language. As an example, in Fig. 4 shows the results of calculating the activity coefficients of the H_2O and D_2O components for atmospheric pressure P = 101.325 kPa and for reduced pressure P = 60 kPa, with a change in the D_2O concentration in the liquid phase from 0 to 100 mol %. The accuracy of calculating the boiling point of the mixture on the plate is $\varepsilon = 10^{-10}$°C.

Based on the appearance of the dependences of the activity coefficients γ_{H_2O} and γ_{D_2O} (Fig. 4), it can be concluded that they are practically straight lines at P = const. This is because the separation coefficient α_{H-D} depends on the pressure and boiling point of the H_2O–D_2O mixture, which changes slightly with a change in the composition of the mixture at P = const. However, with a pressure drop along the height of the column, as shown in [4], the change in the activity coefficients of these components is nonlinear. The values of the activity coefficients of both components are within unity, while the value of the activity coefficient of deuterium oxide γ_{D_2O} is greater than that of hydrogen oxide γ_{H_2O} in the entire range of concentrations. This result is embedded in Eq. (3), in which the separation factor $\alpha_{H-D} > 1$. Also, $\gamma_{D_2O} > 1$, but $\gamma_{H_2O} < 1$, and at concentrations equal to 1, the activity coefficients are also equal to 1.

Activity coefficients γ_{H_2O} and γ_{D_2O}, calculated by the UNIQUAC group composition method.

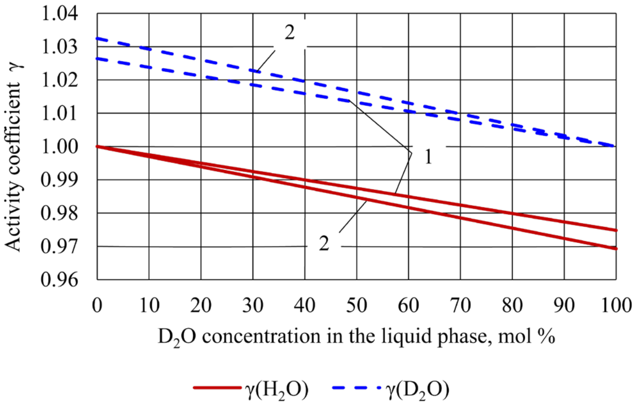


Fig. 4. Dependence of the activity coefficients of the H_2O and D_2O components calculated by Eqs. (1) and (2) on the D_2O concentration in the liquid phase at: (1) P = 101.325 kPa and (2) P = 60 kPa.

The mathematical form is given in [5]: it changes from 0.997 to 1.000 when D_2O changes from 0 to 100 mol % in a mixture of $H_2O–D_2O$. The calculation was carried out at P = 101.325 kPa and P = 60 kPa. Therefore, their values are almost equal to 1, which is typical for ideal mixtures.

The predicted parameters of the binary energy interaction Δu_{12} and Δu_{21} of the UNIQUAC model between the molecules of the H_2O and D_2O components were taken from the database of the Hysys software (Table 3).

Optimizing the parameters of the energy binary interaction Δu_{12} and Δu_{21} of the UNIQUAC model in the range of change from $-\infty$ to $+\infty$ did not lead to an increase in the accuracy of calculating $\alpha_{H–D}$ the $H_2O–D_2O$ mixture. It should be noted that for large values of the binary interaction parameters Δu_{12} and Δu_{21} regardless of their sign, the equilibrium curve in the $x–y$ diagram intersects the diagonal of the square, meaning the presence of an azeotrope point. This is not supported by experimental data and the industrial method for separating a mixture of H_2O and D_2O, i.e., the $H_2O–D_2O$ mixture is not azeotropic. A similar picture was obtained when optimizing the parameters of the NRTL equation (Δg_{12}, Δg_{21}, and α_{12}). Therefore, further calculations give the parameters presented in Table 3.

The calculated value of the separation factor $\alpha_{H–D}$ using the UNIQUAC model at atmospheric pressure was 1.053 (at $x_{H_2O} = x_{D_2O} =$ 0.5 mol %), while the experimental value was 1.026 [16]. The values of the separation factors in the analytical calculation of the activity coefficients γ_{H_2O} and γ_{D_2O} are consistent with the experimental values.

Figure 5 shows the curves of the separation factors, constructed according to Eq. (4) and according to the UNIQUAC method. The vapor pressure of the pure component was calculated using the Antoine equation, the mathematical form of which and the equation constants are given in [4].

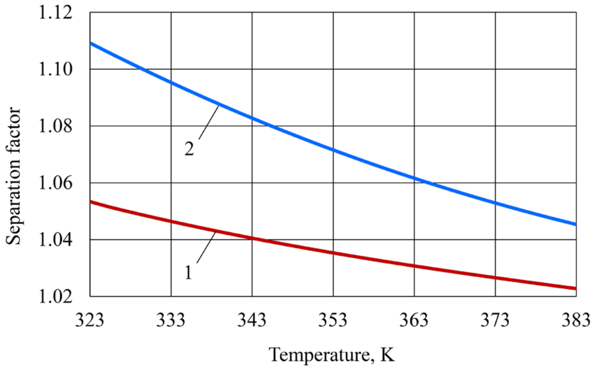


Fig. 5. Dependence of the separation factor on temperature: (1) calculation according to Eq. (4); (2) calculation according to UNIQUAC.

$$\alpha_{H–D} = \sqrt{\frac{P^{\circ}_{H_2O}}{P^{\circ}_{D_2O}}} \tag{4}$$

Thus, when considering the $H_2O–D_2O$ isotopic mixture as ideal, the separation factor $\alpha_{H–D}$ (curve 2, Fig. 5) exceeds the known experimental data considered by us in [17]. This data is consistent with that constructed using Eq. (4) (curve 1, Fig. 5), and coincides with the curve based on the analytical calculation method.

Let us consider the effect of the difference in the separation factor thus defined on the phase equilibrium in the vapor–liquid system of the $H_2O–D_2O$ binary mixture. Let us take the phase equilibrium constant K_{H_2O} as the ratio of the equilibrium molar concentrations of H_2O in the vapor y_{H_2O} and liquid x_{H_2O} phases. We will carry out the calculation based on the UNIQUAC method and Eq. (5).

$$K_{H_2O} = \frac{y_{H_2O}}{x_{H_2O}} = \frac{P^{\circ}_{H_2O}}{P}\gamma_{H_2O}, \tag{5}$$

where γ_{H_2O} will be calculated with Eq. (1) and the separation factor in Eq. (1) is determined by Eq. (4).

Table 3. Parameters of the UNIQUAC model (according to Hysys)

Component	***r***	***q***	**Δu_{12}, cal/mol, H_2O (1)**	**Δu_{21}, cal/mol, D_2O (2)**
H_2O (1)	0.92	1.3997	–	−48.413
D_2O (2)	0.92	1.3998	48.724	–

Note: r and q are volume and area parameters of the components. The energy parameters of the binary interaction Δu_{12} and Δu_{21} are given at the universal gas constant R = 1.98721 cal/(mol·K).

The results of the calculation are shown in Fig. 6 for two pressures P = 101.325 kPa and P = 60 kPa. Data analysis in Fig. 6 shows that with decreasing pressure, the phase equilibrium constant of the highly volatile component H_2O increases, while with an increase in the concentration of H_2O in the liquid phase, it also decreases at x_{H_2O} = 1. The constant is equal to one, which is already known. A change in pressure does not lead to a change in the qualitative picture of the phase equilibrium constant. The shape of the curves is close to linear at P = const. However, when calculating distillation columns, the pressure drop across the column has a significant effect on the nonlinearity of this dependence [4]. The value of the phase equilibrium constant in the calculation by the UNIQUAC method is greater than in the analytical calculation method, which includes the calculation of the separation factor α_{H-D} according to the Urey's Eq. (4). Despite a slight difference in hundredths, this discrepancy, as will be shown below, leads to a significant decrease in the NTSS as determined in Hysys software when calculating the activity coefficients using the UNIQUAC method.

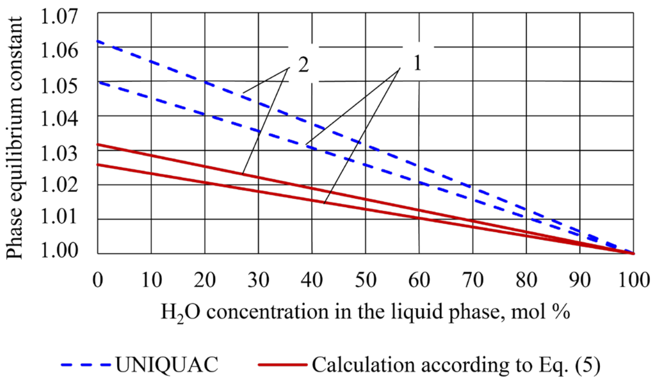


Fig. 6. Dependence of the H_2O phase equilibrium constant on its composition in the liquid phase for the H_2O–D_2O mixture: (1) P = 101.325 kPa; (2) P = 60 kPa.

Thus, the main influence on the phase equilibrium constant is exerted by the vapor pressure of the pure component, which can be determined with a high level of accuracy. We do not recommend taking the activity coefficients of the H_2O and D_2O components equal to 1 into the analytical calculation method, since the H_2O–D_2O mixture is not ideal.

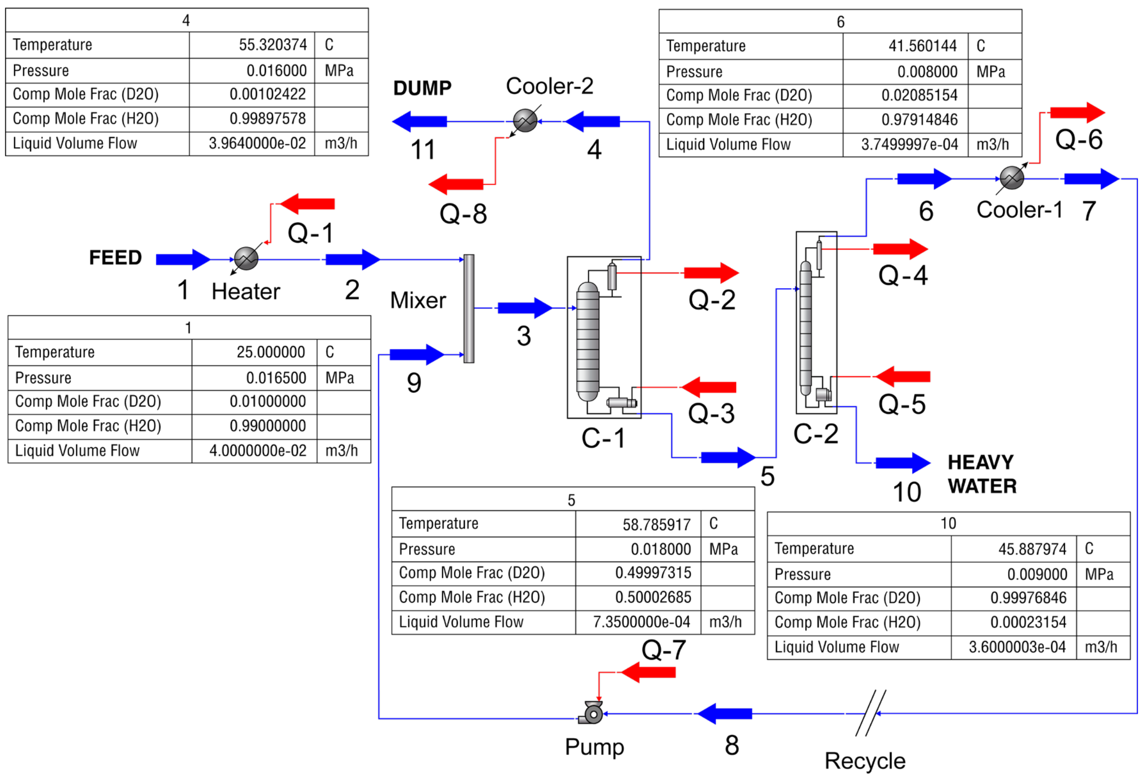
Let us simulate a two-column Kuhn installation in the Hysys software. The block diagram with the calculation results in tabular form in the Hysys graphical software is shown in Fig. 7. The pressure in the upper part of the columns was determined according to Kuhn's experimental data, and is 0.016 MPa (120 mm Hg) for the first stage, 0.008 MPa (60 mm Hg) for the second stage. The pressure in the lower part of the column of the first stage was 0.018 MPa, while the pressure of the second stage was 0.009 MPa. In the column of the first stage, the reflux ratio and the amount of withdrawal of distillate were taken as active specifications; while in the column of the second stage—the reflux ratio and the amount of with drawal of the distillate residue. The calculation of the activity coefficients of the H_2O and D_2O components was performed using the UNIQUAC method. We took the NTSS and the number of the feed plate for each column as identification parameters. The simulation results are given in Table 4 and in the flow tables in Fig. 7.

For the first stage, the NTSS was 86, excluding the reboiler and condenser, the feed plate was numbered 67th. For the second stage, the NTSS was 151; the feed plate was 136th. The TSS values discovered in both columns were 88 and 153, including the reboiler and condenser. These were less than the experimental values (295 and 400) in the Kuhn installation. The D_2O concentration profile was smoother (Fig. 8) compared to the profile shown in Fig. 3. This can be explained by the error in calculating the phase equilibrium constants

Table 4. Material balance of the two-column Kuhn plant in the Hysys environment

Stage number	**Material flows, kmol/day**				**D_2O concentration, mol %**				**R**	**NTSS**	**N_F**
	F	**D**	**W**	**Rec**	**x_F**	**x_D**	**x_W**	**x_{rec}**			
1 stage	2.2159	2.1959	0.04069	0.02077	1	0.10242	49.997	2.0851	25.23	86	67
2 stage	0.04069	0.02077	0.01991	–	49.997	2.0851	99.977	–	74.67	151	136

Note: N_F is the feed plate number; number of theoretical separation stages (NTSS) does not include a reboiler and a dephlegmator condenser.



4		
Temperature	55.320374	C
Pressure	0.016000	MPa
Comp Mole Frac (D2O)	0.00102422	
Comp Mole Frac (H2O)	0.99897578	
Liquid Volume Flow	3.9640000e-02	m3/h

6		
Temperature	41.560144	C
Pressure	0.008000	MPa
Comp Mole Frac (D2O)	0.02085154	
Comp Mole Frac (H2O)	0.97914846	
Liquid Volume Flow	3.7499997e-04	m3/h

1		
Temperature	25.000000	C
Pressure	0.016500	MPa
Comp Mole Frac (D2O)	0.01000000	
Comp Mole Frac (H2O)	0.99000000	
Liquid Volume Flow	4.0000000e-02	m3/h

5		
Temperature	58.785917	C
Pressure	0.018000	MPa
Comp Mole Frac (D2O)	0.49997315	
Comp Mole Frac (H2O)	0.50002685	
Liquid Volume Flow	7.3500000e-04	m3/h

10		
Temperature	45.887974	C
Pressure	0.009000	MPa
Comp Mole Frac (D2O)	0.99976846	
Comp Mole Frac (H2O)	0.00023154	
Liquid Volume Flow	3.6000003e-04	m3/h

Fig. 7. Graphical interface of the Kuhn installation in the Hysys software: C-1, C-2 are distillation columns; 1–11 are material flows; Q-1–Q-8 are energy (heat) flows.

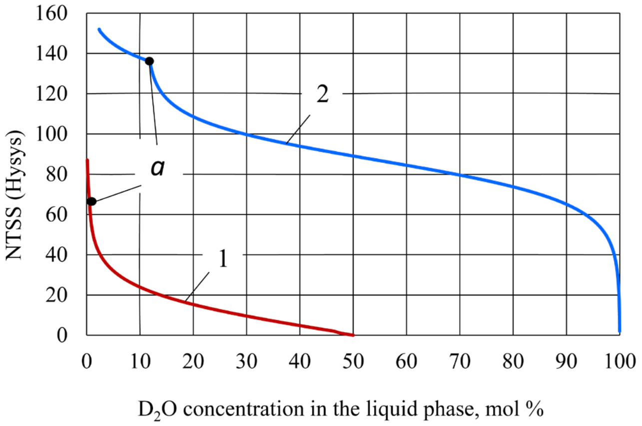


Fig. 8. Profile of change in D_2O concentration along the height of the columns (according to the calculation data in the Hysys simulation software): (1) first stage; (2) second stage.

using the UNIQUAC method. However, the convergence of the material balance for D_2O was $1.38 \cdot 10^{-6}$% and the absolute error of the found values of concentrations in material flows did not exceed 0.12 mol %.

The results obtained indicate that the Hysys software can be recommended when searching for and optimizing the block diagram of a cascade of distillation columns with direct and recycle flows, designed to separate a mixture of H_2O–D_2O. The calculated data obtained in Hysys on the inlet and outlet flows of each column (flow rate, composition, temperature, and pressure) can be used in the analytical program for the calculation of the distillation column to refine the NTSS and the distribution profile of the concentrations of the H_2O and D_2O components along the height of the column.

CONCLUSIONS

The simulation of an experimental two-column Kuhn installation for D_2O production was carried out based on the analytical method for calculating the column, as well as using Hysys simulation software. The calculation of the activity coefficients of the H_2O and D_2O components in the analytical method of calculation was performed according to Eqs. (1) and (2), and in the Hysys software, according to the UNIQUAC equation. Both calculations showed sufficient convergence of calculated and experimental data in material flows. The NTSS found in the Hysys software in both columns, taking into account the reboiler and condenser, are 88 and 153. This is less than the experimental 295 and 400, respectively.

Analysis of the graphical dependences of the activity coefficients γ_{H_2O} and γ_{D_2O} of the H_2O and D_2O components on the D_2O concentration in the liquid phase at P = 101.325 kPa and P = 60 kPa, calculated by Eqs. (1) and (2), showed that $\gamma_{D_2O} > 1$ and $\gamma_{H_2O} < 1$, and at concentrations equal to 1, the activity coefficients are equal to 1. The main influence on the phase equilibrium constant is exerted by the vapor pressure of the pure component, which is determined with a high level of accuracy.

The activity coefficients of the H_2O and D_2O components calculated by the UNIQUAC method at P = 101.325 kPa and P = 60 kPa vary in the range from 0.997 to 1.000. However, both are less than 1, affecting the value of the separation coefficient $\alpha_{H–D}$, which at atmospheric pressure was 1.053 (at $x_{H_2O} = x_{D_2O}$ = 0.5 mole fractions), while the experimental value was 1.026.

An overestimated value of the separation factor $\alpha_{H–D}$ led to an increase in the phase equilibrium constant of H_2O, which affected the NTSS in the column. However, the convergence of the material balance for D_2O is high and amounted to $1.38\cdot10^{-6}$%. The absolute error of the values of concentrations in material flows did not exceed 0.12 mol %.

As a result of the studies, it can be concluded that the Hysys software can be further used to search, analyze, and optimize the operating mode of technological schemes which consist of a cascade (from 2 or more) distillation columns equipped with direct and recycle flows to separate a mixture of H_2O–D_2O, in order to obtain heavy or light water with a given content of deuterium oxide under industrial conditions. After developing the circuit in the Hysys software and determining the operating mode and parameters of the inlet and outlet flows (flow rate, composition, temperature, pressure drop across the column, etc.), the NTSS in the columns must be refined based on an analytical calculation using Eqs. (1) and (2) for the calculation of activity coefficients γ_{H_2O} and γ_{D_2O} of the H_2O and D_2O components, while the profile of changes in the concentrations of the components along the height of the column must also be determined.

Authors' contribution

All authors equally contributed to the research work.

The authors declare no conflicts of interest.

REFERENCES

1. Plotnikova L.V., Chilikova I.I., Sitnikov S.Y., Ukhlin V.E., Efremov G.I., Kislov A.P. Computer model of the power system with inclusion of a heat pump in the process of separation. *E3S Web of Conf*. 2019;124:01032. https://doi.org/10.1051/e3sconf/201912401032

2. Sotelo D., Favela-Contreras A., Lozoya C., Beltran-Carbajal F., Dieck-Assad G., Sotelo C. Dynamic simulation of a crude oil distillation plant using Aspen-Hysys. *Int. J. Simul. Model.* 2019;18(2):229–241. https://doi.org/10.2507/IJSIMM18(2)465

3. Magomedbekov E.P., Belkin D.Yu., Rastunova I.L., Sazonov A.B., Selivanenko I.L., Kulov N.N. Simulation and Optimization of the Deprotiation Cascade of a Heavy-Water Moderator. *Theor. Found. Chem. Eng*. 2017;51(2):133–141. https://doi.org/10.1134/S004057951702004X

[Original Russian Text: Magomedbekov E.P., Belkin D.Yu., Rastunova I.L., Sazonov A.B., Selivanenko I.L., Kulov N.N. Simulation and Optimization of the Deprotiation Cascade of a Heavy-Water Moderator. *Teoreticheskie osnovy khimicheskoi tekhnologii*. 2017;51(2):131–139 (in Russ.). https://doi.org/10.7868/S0040357117020051]

4. Korotkova T.G., Kas'yanov G.I. Calculating a Rectification Column for Separating Mixtures of Light and Heavy Water. *Russ. J. Phys. Chem.* 2021;95(5):1051–1060. https://doi.org/10.1134/S0036024421050186

СПИСОК ЛИТЕРАТУРЫ

1. Plotnikova L.V., Chilikova I.I., Sitnikov S.Y., Ukhlin V.E., Efremov G.I., Kislov A.P. Computer model of the power system with inclusion of a heat pump in the process of separation. *E3S Web of Conf*. 2019;124:01032. https://doi.org/10.1051/e3sconf/201912401032

2. Sotelo D., Favela-Contreras A., Lozoya C., Beltran-Carbajal F., Dieck-Assad G., Sotelo C. Dynamic simulation of a crude oil distillation plant using Aspen-Hysys. *Int. J. Simul. Model.* 2019;18(2):229–241. https://doi.org/10.2507/IJSIMM18(2)465

3. Магометбеков Э.П., Белкин Д.Ю., Растунова И.Л., Сазонов А.Б., Селиваненко И.Л., Кулов Н.Н. Математическое моделирование и оптимизация каскада депротизации тяжеловодного замедлителя. *Теор. основы хим. технологии.* 2017;51(2):131–139. https://doi.org/10.7868/S0040357117020051

4. Короткова Т.Г., Касьянов Г.И. Метод расчета ректификационной колонны для разделения смеси легкой и тяжелой воды. *Журн. физ. химии*. 2021;95(5):800–809. https://doi.org/10.31857/S0044453721050186

5. Уэйлес С. *Фазовые равновесия в химической технологии*: в 2 ч.; пер. с англ. А.В. Беспалова, А.П. Жукова, В.В. Паукова. М.: Мир; 1989. Ч. 1. 301 с. Ч. 2. 360 с.

6. Alshbuki E.H., Bey M.M., Mohamed A.A. Simulation Production of Dimethylether (DME) from Dehydration of Methanol Using Aspen Hysys. *Sch. Int. J. Chem. Mater. Sci*. 2020;3(2):13–18. https://doi.org/10.36348/sijcms.2020.v03i02.002

[Original Russian Text: Korotkova T.G., Kas'yanov G.I. Calculating a Rectification Column for Separating Mixtures of Light and Heavy Water. *Zhurnal fizicheskoi khimii*. 2021;95(5):800–809 (in Russ.). https://doi.org/10.31857/S0044453721050186]

5. Walas S. *Fazovye ravnovesiya v khimicheskoi tekhnologii* (*Phase equilibria in chemical technology*). In 2 v.; transl. from Engl. Moscow: Mir; 1989. V. 1. 301 p. V. 2. 360 p. (in Russ.).

6. Alshbuki E.H., Bey M.M., Mohamed A.A. Simulation Production of Dimethylether (DME) from Dehydration of Methanol Using Aspen Hysys. *Sch. Int. J. Chem. Mater. Sci*. 2020;3(2):13–18. https://doi.org/10.36348/sijcms.2020.v03i02.002

7. Ivanov I.V., Lotkhov V.A., Kulov N.N. Modeling of batch extractive distillation. *Theor. Found. Chem. Eng.* 2017;51(3):253–261. https://doi.org/10.1134/S004057951703006X

[Original Russian Text: Ivanov I.V., Lotkhov V.A., Kulov N.N. Modeling of batch extractive distillation. *Teoreticheskie osnovy khimicheskoi tekhnologii*. 2017;51(3):239–247 (in Russ.). https://doi.org/10.7868/S004035711703006X]

8. Gil I.D., Uyazán A.M., Aguilar J.L., Rodríguez G., Caicedo L.A. Separation of ethanol and water by extractive distillation with salt and solvent as entrainer: process simulation. *Braz. J. Chem. Eng*. 2008;25(01):207–215. https://doi.org/10.1590/S0104-66322008000100021

9. Korotkova T.G., Konstantinov E.N. Modeling technology for food alcohol on distillation plant. *Izvestiya vuzov. Pishchevaya tekhnologiya = Food Technology.* 2012;1(325):108–111 (in Russ.).

10. Jorge L.M.M, Polli P.A., Nicolin D.J., Jorge R.M.M., Paraíso P.R., Filho R.M. Simulation and analysis of an industrial column system of bioethanol distillation heated by vapor direct injection. *ENGEVISTA*. 2015;17(2):254–265. https://doi.org/10.22409/engevista.v17i2.657

11. Korotkova T.G., Konstantinov E.N. Production technology of anhydrous ethyl alcohol azeotropic method. *Izvestiya vuzov. Pishchevaya tekhnologiya = Food Technology.* 2013;1(331):72–76 (in Russ.).

12. Bhattacharyya R, Bhanja K. Studies on the Dynamic Behaviour and Hydraulic Characteristics of a Water Distillation Column. *Chem. Technol. Ind. J.* 2018;13(2):125. URL: https://www.tsijournals.com/articles/studies-on-the-dynamic-behaviour-and-hydraulic-characteristics-of-a-water-distillation-column-13803.html

13. Krell E. *Handbuch der Labaratoriumsdestillation*. Berlin; 1976.

[Krel' E. *Rukovodstvo po laboratornoi peregonke*. (*Handbook on laboratory distillation*) transl. from German. Moscow: Khimiya; 1980. 520 p. (in Russ.).]

14. Vargaftik N.B. *Spravochnik po teplofizicheskim svoistvam gazov i zhidkostei* (*Reference book on thermophysical properties of gases and liquids*). Moscow: Nauka; 1972. 720 p. (in Russ.).

15. Volkov A.I., Zharskii I.M. *Bol'shoi khimicheskii spravochnik* (*Big chemical reference book*). Minsk: Sovremennaya shkola; 2005. 608 p. (in Russ.).

16. Rozenkevich M.B., Rastunova I.L. Theoretical foundations of isotope separation processes. In: *Interaction of Hydrogen Isotopes with Structural Materials*: *Abstracts of presentations at the V International Conference and IX International School for Young Scientists and Specialists*. Sarov; 2015. P. 57–76 (in Russ.). URL: http://book.sarov.ru/wp-content/uploads/2017/12/IHISM-14-5.pdf

7. Иванов И.В., Лотхов В.А., Кулов Н.Н. Моделирование процесса периодической экстрактивной ректификации. *Теор. основы хим. технологии.* 2017;51(3):239–247. https://doi.org/10.7868/S004035711703006X

8. Gil I.D., Uyazán A.M., Aguilar J.L., Rodríguez G., Caicedo L.A. Separation of ethanol and water by extractive distillation with salt and solvent as entrainer: process simulation. *Braz. J. Chem. Eng*. 2008;25(01):207–215. https://doi.org/10.1590/S0104-66322008000100021

9. Короткова Т.Г., Константинов Е.Н. Моделирование технологии получения пищевого спирта на брагоректификационной установке. *Изв. вузов. Пищевая технология*. 2012;1(325):108–111.

10. Jorge L.M.M, Polli P.A., Nicolin D.J., Jorge R.M.M., Paraíso P.R., Filho R.M. Simulation and analysis of an industrial column system of bioethanol distillation heated by vapor direct injection. *ENGEVISTA*. 2015;17(2):254–265. https://doi.org/10.22409/engevista.v17i2.657

11. Короткова Т.Г., Константинов Е.Н. Технология получения безводного этилового спирта азеотропным методом. *Изв. вузов. Пищевая технология.* 2013;1(331):72–76.

12. Bhattacharyya R, Bhanja K. Studies on the Dynamic Behaviour and Hydraulic Characteristics of a Water Distillation Column. *Chem. Technol. Ind. J.* 2018;13(2):125. URL: https://www.tsijournals.com/articles/studies-on-the-dynamic-behaviour-and-hydraulic-characteristics-of-a-water-distillation-column-13803.html

13. Крель Э. *Руководство по лабораторной перегонке*: пер. с нем. М.: Химия; 1980. 520 с.

14. Варгафтик Н.Б. *Справочник по теплофизическим свойствам газов и жидкостей*. М.: Наука; 1972. 720 с.

15. Волков А.И., Жарский И.М. *Большой химический справочник*. Минск: Современная школа; 2005. 608 с.

16. Розенкевич М.Б., Растунова И.Л. *Теоретические основы процессов разделения изотопов. Взаимодействие изотопов водорода с конструкционными материалами. IHISM'14: Сборник докладов Пятой Международной конференции и Девятой Международной школы молодых ученых и специалистов им. А.А. Курдюмова*. Саров: ФГУП «РФЯЦ-ВНИИЭФ»; 2015. С. 57–76. URL: http://book.sarov.ru/wp-content/uploads/2017/12/IHISM-14-5.pdf

17. Korotkova T.G., Kasyanov G.I., Baryshev M.G. Validation for adequacy description of the vapor-liquid phase equilibrium at the theoretical step when separating a mixture of light and heavy water by rectification. *Egyptian J. Chem*. 2022;65(2):591–595**.** https://doi.org/10.21608/ejchem.2021.94114.4433

17. Korotkova T.G., Kasyanov G.I., Baryshev M.G. Validation for adequacy description of the vapor-liquid phase equilibrium at the theoretical step when separating a mixture of light and heavy water by rectification. *Egyptian J. Chem*. 2022;65(2):591–595.

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