Modeling of adsorption process in continuous counter current column having diffused flow structure in gaseous phase

A B Golovanchikov¹, N A Merentsov¹, M V Topilin²

¹Volgograd State Technical University, Volgograd 400005, Russian Federation
²Branch of LUKOIL-Engineering VolgogradNIPlmorneft, Volgograd 400078, Russian Federation

E-mail: steeple@mail.ru

Abstract. The authors have studied the physical and mathematical models of the continuous adsorbing apparatus having diffused flow structure in gaseous phase and ideal displacement in dispersed solid phase of the adsorbent. There have been obtained equations of the operating line and profiles of concentrations of redistributed component in gas and adsorbent particles in its layer height. The authors offer a calculation algorithm and have compared the main technological and geometrical parameters of the studied process with typical adsorption having ideal displacement flow structures in both phases.

1. Introduction
Traditional calculation methods for continuous adsorbing apparatuses are based on counterflow of continuous gaseous phase upwards and of dispersed solid phase of the adsorber downwards; these methods assume that the flow structures of both phases correspond to ideal displacement mode [1-16]. Some papers demonstrate that flow structures can significantly differ from ideal displacement [17, 18]. First of all this refers to gas flows which has low inertia and friction forces due to low density and viscosity; this facilitates their turbulization that results in longitudinal and transversal mixing. However, if the latter contributes to leveling of the velocity profile in the apparatus cross-section, longitudinal mixing results in a considerable change of the concentration background in the apparatuses and reactors along the length and height [19, 20]. When compared with other flow structure models (cell-like or combined) longitudinal mixing is most accurately accounted for in diffused structure models, though they are most mathematically complicated, because they are described by second-order differential equations that usually have no analytical solution.

2. Calculations
We can create an elementary material balance for continuous gaseous phase with diffused flow structure and solid dispersed phase having the flow structure with ideal displacement. For display purposes we can select a height element in dispersed phase dδ between sections I-I and II-II denoting material flows and their concentrations (figure 1).
Figure 1. Scheme showing material flows and concentrations in them of the substance extracted from the gas into the adsorbent at elementary height of the moving adsorbent layer.

\[ \omega S C + \nu_D S + \rho_n S U X = \omega S \left( C - \frac{dC}{dz} \right) + S \left( \nu_D + \frac{d\nu_D}{dz} \right) + U \rho_n S \left( X + \frac{dX}{dz} \right) \]

Here on the left we see the input of the extracted component \( A \) with gas flow rate \( q_v \), back diffusion and adsorbent, and on the right – the rate of the same flows from the selected elementary layer of the adsorbent having a height \( dz \).

Having performed the algebraic manipulations accounting for the velocity of longitudinal diffusions – an analogue of the first Fick law where the molecular diffusion coefficient is replaced by longitudinal diffusion coefficient

\[ \nu_D = -D_l \frac{dC}{dz} \quad (1) \]

we receive the differential equation of the operating line

\[ \frac{U}{\omega \rho_n} \frac{dX}{dh} = Pe \frac{dC}{dh} - \frac{d^2 C}{dh^2} \]

where \( Pe = \omega H / D_l \) – Peclet number of longitudinal diffusion for gas, and \( h = z / H \) – is a dimensionless height of the adsorbent layer, which after integration over the parameter with account of continuity equations \( q_v = \omega S \) and \( G = U S \rho_n \) after integration over parameters we receive an integral expression

\[ \frac{G}{q_v} \left( \int_{X_0}^{X} dX = Pe \int_{C_0}^{C} dC - \int_{g_0}^{g} dg \right) \]

where \( C \) and \( g \) are input concentration and dimensionless gradient of concentration in gas, respectively, which after integration and algebraic manipulations results in the integral equation of the operating line.
We know the boundary condition at the input for the flow described by diffusion model [17, 18] 
\( h=0 \)

\[ C_0 = C_H - \frac{1}{Pe} g_n. \]  

(3)

Then equation of the operating line (2) is reduced to

\[ X = X_k + \frac{q_v}{G} (C - C_n) - \frac{q_v}{G} (g_n - g) / Pe \]  

(2)

Using the material balance equation

\[ G(X_k - X_0) = q_v (C_0 - C_k) \]

we receive out of formula (3) the condition for dimensionless gradient of concentrations of the extracted component in gas

\[ h = 1, g_k = 0. \]  

(5)

The analysis of the received equation of operating line (3) indicates that at \( Pe \to \infty \), i.e. when the flow structure corresponds to ideal displacement mode, too, it is transformed into the known linear equation of the operating line.

We can analytically derive the equation for determination of the dependence between gradient \( g=dC/dX \) and concentration \( C \) and adsorbent layer height.

We can make an elementary material balance by concentration of the component \( C \) extracted from gas at the height of the adsorbent layer \( dz \) (figure 1) with

\[ \omega SC + \nu_D S = \omega S (C - \frac{dC}{dz}) + S (\nu_D + \frac{d\nu_D}{dz}) + K_F S \sigma dz (C - C^*). \]

After algebraic manipulations with account of formula (1) we can receive differential equation

\[ D_l \frac{d^2 C}{dz^2} = \omega \frac{dC}{dz} - K_v (C - C^*), \]

which in dimensionless view is transformed into

\[ \frac{d^2 C}{dh^2} = Pe_i \frac{dC}{dh} - K_v \tau_e Pe (C - C^*) \]  

(6)

with gradient conditions at the input (3), at the output

\[ h = 1, C = C_k. \]  

(7)

Formula (6) is referred to second-order differential equations which in general view have no analytical solution.

However, if equilibrium line is described by linear equation

\[ C^* = \frac{AX}{B}, \]  

(8)

which with account of the equation of the operation line (4) is transformed into
Then differential equation (6) with account of the latter expression and algebraic modifications [21] becomes

\[
C'' - PC' - qC = R
\]

where

\[
P = Pe_i + K_c \tau_c (q_v / G) / B, \quad q = K_c \tau_c Pe_i \left[1 - (q_v / G) / B\right], \quad R = K_c \tau_c Pe_i \left[(q_v / G)C_0 - X_k \right] / B,
\]

and is referred to linear second-order differential equations with constant coefficients and with the right part that has an analytical solution which was first time considered when modeling adsorption processes [22, 23]

\[
C = C_1 \exp(r_1 h) + C_2 \exp(r_2 h) + Q
\]

where \(r_{1,2} = +P/2 \pm \sqrt{(P/2)^2 + q}\).

Constant integration \(C_i\) and \(C_2\) of the general solution of a homogeneous differential equation can be received from boundary conditions (5) and (7)

\[
C_k = C_1 \exp(r_1) + C_2 \exp(r_2) + Q, \quad C_1 r_1 \exp(r_1) + C_2 r_2 \exp(r_2) = 0
\]

specific solution \(Q\) of differential equation (9) has the view

\[
Q = -R/q,
\]

and constant integrations are described by expressions

\[
C_1 = (C_k - Q) \exp(-r_1) / (1 - r_1 / r_2); \quad C_2 = -C_1 (r_1 / r_2) \exp(r_1 - r_2).
\]

Table 1. Initial and reference data and calculation parameters of continuous adsorbing apparatus [3].

| No | Parameter | Dimension | Symbol | Value |
|----|-----------|-----------|--------|-------|
| 1  | Capacity for the air cleaned from methanol vapours | m³/h | \(q_v\) | 7.340 |
| 2  | Initial concentration of methanol vapours in air | kg A/ m³ | \(C_0\) | 0.0018 |
| 3  | Degree of purification | - | \(\eta\) | 0.95 |
| 4  | Operation temperature | °C | \(t\) | 20 |
| 5  | Equivalent diameter of adsorbent particles | m | \(d_e\) | 0.002 |
| 6  | Loose density of the adsorbent particles | kg/ m³ | \(\rho_l\) | 550 |
| 7  | Density of air at operation temperature and atmospheric pressure | kg/ m³ | \(\rho_n\) | 1.2 |
| 8  | Pressure in the adsorbing apparatus | atm | \(p\) | 1.033 |
9 Pore volume of the adsorbent particles in the moving layer \( m^3/m^3 \) \( \varepsilon_0 \) 0.375

10 Air viscosity at operation temperature of the air \( \text{pas} \) \( \mu \) 1.8 \( \cdot \) 10^{-5}

11 Proportionality factor of the equilibrium line \( m^3/kg \) \( B \) 18.33

12 Diffusion coefficient of methanol vapours in air at operation temperature and pressure \( m^2/s \) \( D_y \) 1.43 \( \cdot \) 10^{-3}

13 Diffusion coefficient of methanol vapours in air at operation temperature and pressure \( m^2/s \) \( D_x \) 3 \( \cdot \) 10^{-10}

### Variables

| 1 | Peclet number for longitudinal diffusion for air | - | Pe | 30 |

| Calculated parameters |

| 1 | Calculated velocity of air \( m/s \) | \( \omega_{calc} \) | 2.91 \( \cdot \) 10^{-1} |
| 2 | Standard diameter of the adsorbent \( m \) | \( D_a \) | 3 |
| 3 | Fictitious velocity of air \( m/s \) | \( \omega \) | 2.89 \( \cdot \) 10^{-1} |
| 4 | Reynolds number for air | | 38.5 |
| 5 | Prandtl number diffused | | 1.05 |
| 6 | Nusselt number diffused | | 9.98 |
| 7 | Outer mass transfer coefficient from air to the surface of particles \( m/s \) | \( \beta_y \) | 7.14 \( \cdot \) 10^{-2} |
| 8 | Equilibrium concentration of methanol vapours corresponding to their initial concentration in the air \( kgA/kg \) | \( X_0^* \) | 3.3 \( \cdot \) 10^{-2} |
| 9 | Inner mass transfer coefficient from surface of the particles into micropores \( m/s \) | \( \beta_x \) | 2.42 \( \cdot \) 10^{-2} |
| 10 | Mass transfer coefficient \( m/s \) | \( K_F \) | 1.81 \( \cdot \) 10^{-2} |
| 11 | Specific surface of the particles \( m^2/m^3 \) | \( S_i \) | 1.875 |
| 12 | Volume factor of mass transfer \( 1/s \) | \( K_Y \) | 33.88 |

### Typical calculation of continuous adsorbing apparatus with the structure of ideal displacement of flows in both phases

| 1 | Final concentration of methanol vapours in air at the output of the adsorbing apparatus \( kgA/m^3 \) | \( C_k \) | 9 \( \cdot \) 10^{-5} |
| 2 | Final concentration of methanol in adsorbent particle at the output of the adsorbing apparatus \( kgA/kg \) | \( X_k \) | 3 \( \cdot \) 10^{-2} |
| 3 | Initial concentration of methanol in adsorbent particle at the input to the adsorbing apparatus (after regeneration of the absorber) \( kgA/kg \) | \( X_0 \) | 8.25 \( \cdot \) 10^{-4} |
| 4 | Mass flow rate of the adsorbent \( kg/h \) | \( G \) | 430 |
| 5 | Volume flow rate of the adsorbent \( m^3/h \) | \( q_x \) | 0.781 |
| 6 | Number of transfer units by air | - | \( S_m \) | 18.68 |
| 7 | Height of the adsorbent layer \( m \) | \( H_s \) | 0.159 |
| 8 | Velocity of adsorbent particles \( m/s \) | \( U \) | 3.07 \( \cdot \) 10^{-5} |
| 9 | Time of presence of the air cleaned from methanol vapours in the adsorbent layer \( s \) | \( t_c \) | 0.551 |
| 10 | Time of presence of the adsorbent particles in the tower \( s \) | \( t_x \) | 5176.7 |

### Calculation of continuous adsorbing apparatus with account of the reduction of mass transfer driving energy from longitudinal mixing

| 1 | Coefficient accounting for longitudinal mixing \( m/s \) | \( \beta_l \) | 5.84 \( \cdot \) 10^{-2} |
| 2 | Coefficient of mass transfer with account of longitudinal mixing \( m/s \) | \( K_{Fl} \) | 1.38 \( \cdot \) 10^{-2} |
| 3 | Volume coefficient of mass transfer with \( 1/s \) | \( K_{vl} \) | 25.88 |
account of longitudinal mixing

|   |   |   |   |
|---|---|---|---|
| 4 | Height of the adsorbent layer | m | \( t_d \) | 0.208 |
| 5 | Time of presence of the air cleaned from methanol vapours in the adsorbent layer | s | \( t_{cl} \) | 0.721 |
| 6 | Time of presence of the adsorbent particles in the tower | s | \( t_{dx} \) | 6.677.3 |

Calculation of adsorbent with diffused flow structure by gaseous phase

|   |   |   |   |
|---|---|---|---|
| 1 | Average time of presence of the cleansed air in the adsorbent layer | s | \( t_d \) | 1.31 |
| 2 | Concentration of methanol vapours at the input to the adsorbent layer | kgA/ m\(^3\) | \( C_n \) | 1.706·10\(^{-3}\) |
| 3 | Final concentration of methanol in the layer of the absorbent at the output of the tower | kgA/ m\(^3\) | \( X_k \) | 3·10\(^{-2}\) |
| 4 | Equilibrium concentration of methanol in the adsorbent layer corresponding to its input concentration \( C_n \) into the adsorbent | kgA/ m\(^3\) | \( X_n^* \) | 3.127·10\(^{-2}\) |

5 Coefficients for calculation of equation parameters

|   |   |   |   |
|---|---|---|---|
| - | \( r_1 \) | 72.59 |
| - | \( r_2 \) | -1.261 |
| kgA/ m\(^3\) | \( C_1 \) | 3.32·10\(^{-3}\) |
| - | \( C_2 \) | 2.27·10\(^{-3}\) |
| - | \( P \) | 71.33 |
| kgA/ m\(^3\) | \( Q \) | 91.54 |
| kgA/ m\(^3\) | \( R \) | 5.167·10\(^{-2}\) |
| kgA/ m\(^3\) | \( Q \) | -5.64·10\(^{-2}\) |

| 6 | Height of the adsorbent layer | m | \( H_d \) | 0.378 |
| 7 | Time of presence of the adsorbent particles | s | \( t_{dx} \) | 12.298.8 |

3. Results and Discussion

Table 1 summarizes the initial and reference data and the results of calculation of basic parameters of adsorbing apparatus with ideal displacement flow structure in both phases and of adsorbing apparatus with ideal displacement in dispersed adsorbent phase and diffused flow structure by continuous gaseous phase. For illustration there are initial data for adsorption cleaning of air from methanol vapours [3], and calculation formulae for continuous adsorbing apparatus with counterflow of the solid and gaseous phases are cited from reference books [2, 4].

As it is demonstrated in Table 1 with Pe\(_l\)=30 the required height of the moving adsorbent layer with account of longitudinal diffusion should be increased from \( H_e=0.159 \) m (typical calculation of continuous adsorbing apparatus with the structure of ideal displacement of flows in both phases) to \( H_d=0.378 \) m, i.e. 2.38 times as much. Reference book [3] accounts for longitudinal mixing using longitudinal mixing coefficient which results in the reduction of mass transfer volume coefficient \( K_v=33.88 \) s\(^{-1}\) to 25.88 s\(^{-1}\) and, consequently, increase of the layer height from \( H_e=0.159 \) m to \( H_d=0.208 \) m, i.e. by 30.8%.

Our example of adsorbing apparatus calculation with account of Peclet number diffused \( Pe_l=30 \) the layer height should equal not \( H_d=0.208 \) m, but \( H_d=0.378 \) m, i.e. it does not depend of the fixed value of \( \beta_l \) coefficient that accounts for longitudinal mixing, but on \( Pe_l \) number. Figure 2 shows equilibrium and operating lines; 2 – for adsorbing unit with ideal displacement for both phases and 3 – for ideal displacement for the adsorbent and diffused flow structure by air. As it is showed in the diagrams the diffusion model for the adsorbent results first of all in a leap in methanol concentrations and its
reduction from $C_0$ to $C_n$, and, secondly, operating line 3 becomes curved, not straight 2 as it is usual in mass exchange processes. This results in the necessity to increase the height of the adsorbent layer, because operating line 3 comes close to line 1 that reduces the local and average driving energy. Even more clearly the influence of longitudinal diffusion and $Pe$ number can be seen in the diagrams of methanol concentration profile by relative height of the adsorbent (figure 3).

![Figure 2.](image2.png)

**Figure 2.** Equilibrium line (1) – equation (8), operating line (2) of a typical adsorbing apparatus with ideal displacement in both phases; operating line (3) with ideal displacement flow structure by adsorbent particles and diffused flow structure by cleaned air – equation (4) ($Pe=30$, $G=430$ kg/h).

![Figure 3.](image3.png)

**Figure 3.** Profiles of methanol concentrations by relative height of the adsorbent layer: 1 – diffused flow structure ($Pe=30$) by air; 2 – ideal displacement ($Pe\to\infty$); a – in air; b – in adsorbent.
Dependence between the height of the adsorbent layer and initial concentration of methanol vapours in the air and Pe number is illustrated in figure 4.

Figure 4. Relation between the height of the adsorbent layer and initial concentration of methanol vapours and Peclet number diffused.

This figure and figure 2 show that at $Pe \to 20$, when $C_n^* = 1.64 \cdot 10^{-3} \text{kgA/m}^3$ operating line 3 transects the equilibrium one at the adsorbent flow rate $G = 430 \text{kg/h}$ height of the adsorbent layer $H_d \to \infty$. In this case it is necessary to increase the adsorbent flow rate and, consequently, reduce its final concentration to keep the operating line higher than the equilibrium line (figure 2).

4. Conclusions
Thus, the account of reversed mixing of gas in continuous adsorbing apparatuses results in an abrupt increase of vapour concentrations of the extracted component in gas at the input to the tower, transforms straight operating line into a curved one that decreases the driving energy of mass transfer and requires the increase of the adsorbent layer, as in works [24, 25].

Besides, for each adsorbent flow rate there is a critical value of the Peclet number $Pe^*$ diffused, at which the operating line transects the equilibrium one, and for removal of this effect it is necessary (as in the calculations of a typical adsorbing apparatus with ideal displacement in both phases) to increase the flow rate of the adsorbent and reduce the final concentration in it of the extracted component.

References
[1] Kasatkin A G 2008 The main processes and devices of chemical technology (Moscow: Alians) p 750
[2] Pavlov K F 2013 Examples and problems for the course on processes and apparatuses of chemical technology (Moscow: Alians) p750
[3] Timonin A S 2013 Engineering and ecological reference book 1 (Kaluga) p 917
[4] Dytynerskiy Y I 2008 Basic processes and apparatuses of chemical technology (Moscow: Alians) p 494
[5] Buyantuev S L, Stebenkova Y Y, Khmelev A B, Kondratenko A S and Shishulkin S Y 2017 Journal of Physics: Conf. Series 830 012157
[6] Laguntsov N I, Kurchatov I M, Korolev M V and Tishin A A 2016 Journal of Physics: Conf. Series 751 012041
[7] Golovanchikov A B, Balashov V A and Merentsov N A 2017 Chem. and Pet. Eng. 53 10
[8] Reatto L, Nava M, Galli D E, Billman C, Sofo J O and Cole M W 2012 Journal of Physics: Conf. Series 400 012010
[9] Fukuda A, Terasawa D, Ohno Y and Matsumoto K 2014 Journal of Physics: Conf. Series 568 052009
[10] Rodriguez S J, Albanesi E and Makinistian L 2016 Journal of Physics: Conf. Series 705 012012
[11] Golovanchikov A B, Merentsov N A and Balashov V A 2013 Chem. and Pet. Eng. 48 595
[12] Rozanov L N 2016 Journal of Physics: Conf. Series 729 012001
[13] Shiryaev A A, Voloshchuk A M, Averin A A, Artamonova S D and Volkov V V 2017 Journal of Physics: Conf. Series 848 012009
[14] Di Marco P and Filippeschi S 2012 Journal of Physics: Conf. Series 395 012139
[15] Surzhikov S T 2017 Journal of Physics: Conf. Series 815 012004
[16] Merentsov N A, Bokhan S A, Lebedev V N, Persidskiy A V and Balashov V A 2018 Materials Science Forum 927 183
[17] Levenshpiil O 1966 Engineering description of chemical processes (Moscow: Khimiya) p 621
[18] Kafarov V V 1985 Cybernetics methods in chemistry and chemical technology (Moscow: Khimiya) p 448
[19] Tyabin N V and Golovanchikov A B 1983 Cybernetics methods in rheology and chemical technology (Volgograd: Volgogradskayapravda) p 103
[20] Golovanchikov A B and Dulkina N A 2009 Modeling of the flow structures in chemical reactors. Thesisinpublication (Volgograd: VolgGTU) p 240
[21] Vygotskiy M Y 1966 Reference book on advanced mathematics (Moscow: Nauka) p 424
[22] Ramm V M 1976 Adsorption of gases (Moscow: Chemistry) p 656
[23] Miyauchi T, Vermeulen T 1963 Ind. End. Chem. Fundament 2(2) 113
[24] Golovanchikov A and Merentsov N 2019 Advances in Intelligent Systems and Computing 983 635
[25] Golovanchikov A and Merentsov N 2019 Advances in Intelligent Systems and Computing 983 645