Use of two-stage membrane countercurrent cascade for natural gas purification from carbon dioxide

I M Kurchatov, N I Laguntsov and M D Karaseva

1 National Research Nuclear University MEPhI (Moscow Engineering Physics Institute), Kashirskoe highway 31, Moscow, 115409, Russia
2 JSC Aquaservice, Kashirskoe highway 31, Moscow, 115409, Russia

E-mail: rita09karaseva@mail.ru

Abstract. Membrane technology scheme is offered and presented as a two-stage countercurrent recirculating cascade, in order to solve the problem of natural gas dehydration and purification from CO₂. The first stage is a single divider, and the second stage is a recirculating two-module divider. This scheme allows natural gas to be cleaned from impurities, with any desired degree of methane extraction. In this paper, the optimal values of the basic parameters of the selected technological scheme are determined. An estimation of energy efficiency was carried out, taking into account the energy consumption of interstage compressor and methane losses in energy units.

1. Introduction

According to data published in the Annual Statistical Bulletin 2015, natural gas production in Russia in 2014 was amounted to 643 billion m³/year [1]. With the aim of providing a number of export sales, using of natural gas as an alternative fuel and gas-supplying of settlements, remoted from gas pipeline, natural gas is liquefied.

Natural gas in addition to methane homologues according to their fields may include a variety of impurities, such as helium, hydrogen, argon, nitrogen, hydrogen dioxide, water vapour and other. Carbon dioxide is badly soluble in hydrocarbons. At temperatures and pressures, generated during the liquefaction of natural gas, carbon dioxide forms carbonic ice. Under the process of liquefaction, water vapour containing in the natural gas organises hydrates with hydrocarbons, which in turn affects adversely on the service life of liquefaction system. Thus, it is necessary to produce natural gas dehydration and purification of CO₂. Acceptable levels of carbon dioxide and water vapour in the natural gas are 0.01% and 0.0001%, respectively.

In order to solve the problem of drying and purification of natural gas from the carbon dioxide, a two-stage double circuit countercurrent cascade was considered and the optimal values of its basic parameters were determined.

2. Statement of the problem

On the assumption with the methane permeability through the membrane is \( \pi ( \text{CH}_4) = 1 \ \text{l/atm*h*m}^2 \) and carbon dioxide permeability is \( \pi ( \text{CO}_2) = 40 \ \text{l/atm*h*m}^2 \), the ratio of carbon dioxide permeability
to the methane permeability (selectivity) corresponds to a modified polyimide membrane. Water vapour permeability of view is the same as carbon dioxide permeability.

The pressure value of the feed flow pressure of the module is 40 atm., pressure of the permeate flow is 1 atm., operating temperature is 297K. Productivity of technological scheme, using for gas drying and purification is 140 m$^3$/h (100 kg/h).

3. Results and discussion

In this work the results of numerical studies of the two-stage dual-stage counter-current scheme (Figure 1) are presented for the separation of a ternary mixture of methane (the main component of natural gas), carbon dioxide and water vapour. This stage can be used for natural gas purification by CO$_2$ [2], and He [3],[4], and its energy efficiency substantiated in [3].

\[ C_F(CH_4) = C_{F1}(CH_4) = C_{R3}(CH_4) \]  
\[ C_F(CO_2) = C_{F1}(CO_2) = C_{R3}(CO_2) \]  
\[ C_F(H_2O) = C_{F1}(H_2O) = C_{R3}(H_2O) \]

For the calculation of the first stage (. Figure 1 module 1) the following parameters were set: membrane permeability for the mixture components, R1 is equal to the product flow of 140 m$^3$/h, the concentration of methane (99.99% vol.), carbon dioxide (0.01 vol.) and water vapour (0.0001%) in it,

\[ F \rightarrow F_1 \rightarrow R_1 \]

\[ F \rightarrow R_3 \rightarrow P_3 \]

\[ P_2 \]

\[ P_1 \]

\[ K_1 \]

\[ K_2 \]

\[ I \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]

\[ \]
the value of the high pressure \( p_h = 40 \text{ atm.} \) and low pressure \( p_l = 1 \text{ atm.} \), concentration of the components in the initial mixture into feed flow of the cascade: methane - 97.49\%, carbon dioxide - 2.50\%, and water vapour - 0.01\%.

Calculation of the first stage (ordinary divider) was conducted, using «cross flow» model [5]. It was assumed that the pressure in the low pressure chamber is constant throughout the entire length of the module \( p_l=\text{const} \), the permeability for component \( i \) is constant throughout the entire length of the module \( \pi_i=\text{const} \), gas temperature is constant \( T=\text{const} \), \( \Delta p_h/p_h << 1 \).

Equation of flow balance for the first stage:

\[
F_1 = P_1 + R_1 \tag{4}
\]

Equation of the balance of the component \( i \):

\[
C_{F_1}^i = \theta_1 C_{P_1}^i + (1 - \theta) C_{R_1}^i \tag{5}
\]

where \( \theta_1 \) – flow partition coefficient of the module 1, defined as the ratio of permeate flow of the module to the feed flow of the module:

\[
\theta_1 = \frac{P_1}{F_1} \tag{6}
\]

Selectable volume was chosen for the calculation of the membrane module in a high-pressure chamber, which includes flow \( q \) with a concentration \( C_q^i \) of component \( i \). Partial flow \( Z_i = q \cdot C_q^i \) and concentration of the component \( i \), penetrated through the membrane \( C_l^i \) were determined from the system of equations:

\[
\begin{cases}
\frac{d(Z_i)}{ds} = -\pi_i p_h (C_q^i - \gamma^* C_l^i) \\
C_l^i = \frac{\pi_i (C_q^i - \gamma^* C_l^i)}{\sum_j \pi_j (C_q^j - \gamma^* C_l^j)}
\end{cases} \tag{7}
\]

where \( \gamma^* = p_l/p_h \), \( p_l \) – pressure value in low-pressure chamber, \( p_h \) – pressure value in high-pressure chamber.

Boundary conditions of given system are:

\[
Z_i(s = 0) = FC_P^i \tag{8}
\]

\[
Z_i(s = S) = RC_R^i \tag{9}
\]

The system of the equations was solved by Runge-Kutta method of the fourth order. Concentrations in high-pressure chamber \( C_q^i \) and flow \( q \) were determined from equations:

\[
q = \sum_j Z_j^i \tag{10}
\]

\[
C_q^i = \frac{Z_i^i}{\sum_j Z_j^i} \tag{11}
\]

The second step is a sequential two-module recirculating divider consisting of the modules 2 and 3. The permeate flow \( P_1 \) of the first stage, combining the recirculating flow with the second step \( P_3 \), consists the feed flow of the module 2 (see Figure 1.). The flow, which did not penetrate through the membrane of the second module, inputs to the module 3. The permeate flow \( P_2 \) of the second module is equal to a retentate flow. Flow, which didn’t permeate through the membrane of the third module, is combined with the feed flow \( F \) of the technological scheme.

The following parameters were set for calculating the second stage: temperature of the gas permeability of the membrane for carbon dioxide, methane and water vapour (the same as for the first-stage module), the value of the high pressure \( p_h = 40\text{ atm.} \) and low pressure \( p_l = 1 \text{ atm.} \), feed flow of the second stage is equal to a permeate flow of the first stage \( P_1 \). Concentrations of carbon dioxide, water vapour and methane in the feed flow of the second stage also were set, basing on the obtained
concentrations in the permeate flow of the first stage. Methane concentration in the flow - C_{R3}(CH_4)
methane extraction degree of the second stage φ(CH_4)_2 were set. Methane extraction degree is
calculated by the equation:

$$\phi(CH_4)_2 = \frac{R_3 C_{R3}(CH_4)}{P_1 C_{P1}(CH_4)} \times 100\%$$

Taking into account the balance equation for total flows:

$$P_1 = P_2 + R_3$$

Equation (12) can be expressed this way:

$$\phi(CH_4)_2 = \left(1 - \frac{P_2}{P_1}\right) \times \frac{C_{R3}(CH_4)}{C_{P1}(CH_4)} \times 100\%$$

Flows P_2 and R_3 are determined from equations (13), (14).
Calculation of membrane modules 2 и 3 was performed similarly to membrane module 1 (similarly
to the first stage) using model «cross flow» model. The amount of substance which has entered into
the second module F_{2i}C_{F2i}, is determined by the equation:

$$F_{2i}C_{F2i} = P_1 C_{P1i} + P_3 C_{P3i}$$

An initial approximation of the amount of substance F_{2i}C_{F2i} was set, entered the second module.
Based on this value according to the equations (7), the second module is calculated with a
predetermined value θ_2 approaches the split ratio. Thus, the flow of the third module and component
concentrations in streams P_2 and the third module was determined. To determine the partition
coefficient θ_3 of the third module, the permeate flow of the third module P_3 and concentrations of the
components in it, system of differential equations (7) with the boundary condition was solved:

$$Z_i(s = S) = R_3 C_{R3i}(CH_4)$$

Then the system (15) was solved by Newton’s method. Then recalculate was performed for the
second module, wherein the flow partition coefficient θ_3 defined by the method of relaxation as long
as the desired degree methane extraction was achieved. As a result of performed calculations all
module parameters were determined, were carried out with the complete flow balance equation (13)
and the balance equation for the components of the mixture for the second step:

$$C_{P1i} = \frac{P_3}{P_1} C_{P2i} + \frac{P_2}{\theta_2 P_3} (1 - \theta_2)(1 - \theta_3)C_{R3i}$$

Feed flow of the cascade F is determined by the equation:

$$F = F_1 - R_3$$

Methodology presented in [3] is applied for analysing of energy consumption of the scheme.
According to this technique, the power consumption K_1 - W_1 [kW] of interstage compressor is
calculated, the loss of methane in energy units is accounted and the total energy of given technological
scheme is determined.

Calculation of energy consumption K_1 of interstage compressor was carried out in the
approximation of adiabatic compression:

$$W_1 = \frac{(P_{1i} + P_3) \eta_{ac} \kappa}{\eta_{ac} \kappa - 1} RT \left[ \frac{p_h}{p_i} \right]^{\frac{\kappa - 1}{\kappa}} - 1$$

where P_{1i} + P_3 – compressed flow, [mole/s]; R – universal gas constant [J/mole*K]; T=297ºK – gas
temperature, [K]; \(\kappa=1.32\) - adiabatic index for natural gas, \(\eta_{ac}=0.85\) Efficiency factor of compressor
operating in an adiabatic compression mode; \(p_h\) – flow pressure at the outlet of the compressor equals
to 40 atm., \(p_i\) - flow pressure at the compressor inlet to 1 atm. As a natural gas is a real gas in term
(19), gas compressibility coefficient $\mu = 0.87\, 297^\circ\text{K}$ was accounted for at a temperature and a pressure of 40 atm. [7].

It is important to consider the energy that can be produced by combustion of methane in the permeate flow entered the second stage $P_2$ (retentate flow of the scheme) in the gas turbine. Such energy was named: methane loss in energy units $W_P$ [KW] and was calculated by equation:

$$W_P = P_2 C_{P2} \eta_{GT} Q$$

(20)

Where $P_2$ is a permeate flow of the second module (fig.1), mole/s; $C_{P2}$ – methane concentration in the flow $P_2$; $\eta_{GT}=0.35$ – gas turbine efficiency factor; $Q=800$ kJ/mole – methane combustion heat.

The total energy consumption for the given technological scheme on 1kg of product gas (natural gas in permeate flow) $E$ [kWh / m$^3$] is equal to:

$$E = (W_1 + W_P)/R_1$$

(21)

where $R_1$ - product stream, according to the task, it is 140 Nm$^3$ / h and contains 99.99% methane.

Under realizing calculations of the second stage degree of extraction of methane $\varphi$ (CH$_4$) was varied in the range from 2 95.50% to 99.99%. At methane extraction degree of the second stage 95% recirculation circuit becomes a single divider [3].

On the Fig. 2 the dependence of total reduced energy consumption to methane extraction degree of technological scheme at compressor operation mode, working in an adiabatic compression, is shown. Recalculation of the recovery is carried out according to the formula (22) basing on equation (18):

$$\varphi(CH_4) = \frac{R_1C_{R1}(CH_4)}{(F_1-R_3)C_{F}(CH_4)} \times 100\%$$

(22)

Varying the methane extraction degree of the second stage allows varying methane extraction degree of the whole scheme.

**Figure 2.** The dependence of the total reduced energy consumption to the degree of extraction of the technological scheme of methane, 1 - energy consumption of compressor K1; 2 - methane loss in energy units; 3 - total reduced energy consumption.

Reduced total energy consumption are low and are determined by competitive factors - the growth of energy consumption of the compressor $K_1$ and decrease of methane losses with the rise of extraction degree. Thus, the energy consumption at the minimum with all energy costs is 84.1 Wh/m$^3$. This value for given pressure depends on the ratio of permeability and is independent of their specific values.

Interestingly, the ratio of the concentrations of carbon dioxide and water vapour in the permeate stream and feeding are equal:

$$\frac{C_{CO2}^P}{C_{H2O}^P} \approx \frac{C_{CO2}}{C_{H2O}}$$

(23)
Equation (23) based on equal permeability of carbon dioxide and water vapour, and low concentration of water vapour contained in initial feed gas. Importantly, in this case carbon dioxide, and water vapor may be considered as one component, and the initial concentration of the component is defined as the sum of the concentrations of carbon dioxide and water vapour.

Conclusions
In this paper we considered the problem of drying and purification of natural gas from carbon dioxide, using two-stage double circuit countercurrent membrane cascade. The technique for calculating of this stage was presented. The optimal values of the basic parameters of such a process were determined under given initial parameters.

References
[1]. OPEC Annual Statistical Bulletin Organization of the Petroleum Exporting Countries
[2]. Cnop T, Doong S J, Farr D and Xomeritakis J K 2012 US Patent 2012050816.
[3]. Laguntsov N I, Kurchatov I M, Karaseva M D and Solomakhin V I 2014 Petrol. Chem. 8 673.
[4]. Solomakhin V I, Laguntsov N I, Kurchatov I M and Davydov Y S 2014 RF Patent 150520.
[5]. Laguntsov N I, Talantseva E V and Teplyakov V V 1997 Theor. Found. Chem. Eng. 31 463.
[6]. Laguntsov N I, Gruzdev E B, Kosykh E V and Kozhevnickov V Y 1992 J. Membr. Sci. 67 15-28.
[7]. Stull D R, Westrum Jr E F, Sinke G C 1987 The Chemical Thermodynamics of Organic Compounds (Robert E. Krieger publishing company: Malabar Florida).