2015 • 5

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Results of experimental researches the energy-saving technology of biogas purification for the purpose of obtaining highly concentrated methane

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Key words: Biogas, microbubling equipment, tubular ceramic membranes, highly concentrated methane, unconventional energy sources, mathematical simulation, mass transfer, liquid, gas, microbubbles.

Abstract. The developed technology biogas purification from carbon dioxide gas is proposed. Mass transfer in finely dispersed gas-liquid systems is experimentally investigated. Fine gas-liquid dispersions were created by means of microbubbling method through tubular microfiltering ceramic membranes using incoming liquid. Processes of absorption and chemisorption during microbubbling in mobile liquid phase are studied. Mass transfer coefficients are identified, specific interphase surfaces and interphase flows in microbubbling device during absorption of carbon dioxide from its mixtures with methane and water suspension of CaO are identified. The adequacy of model is proved by experiments of the authors and comparisons with reference experimental data. It is demonstrated, that value specific interphase surface during microbubbling is 8-30 times higher, than in the normal bubbling, which leads to a significant reduction in working volume of a device with the same efficiency. A comparison with membrane hollow fiber contactors shows that using of ceramic membranes allows to substantially increase value specific interphase flow in the microbubbling device and it is comparable or higher than in a case of hollow fiber contactor.

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Результаты экспериментальных исследований энергосберегающей технологии очистки биогаза с целью получения высококонцентрированного метана

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Ключевые слова: Biogas, microbubling equipment, tubular ceramic membranes, highly concentrated methane, unconventional energy sources, mathematical simulation, mass transfer, liquid, gas, microbubbles.

Аннотация. С точки зрения межфазного массообмена объектами исследования являлись зависимости межфазного мольного потока поглощаемого вещества, коэффициентов массоотдачи в газовой и жидкой фазах, а также удельной поверхности контакта фаз от скорости жидкости в мембранном модуле и от концентрации активной части поглотителя. Целью экспериментов являлось получение данных для оценки эффективности межфазного массообмена в мембранном микробарботажном контакторе и сравнении его с массообменными аппаратами других типов.

В результате экспериментов по исследованию межфазного массообмена были получены зависимости удельной поверхности контакта фаз в аппарате и коэффициента массоотдачи в газовой фазе от скорости жидкости в канале мембраны, а так же определена величина межфазного потока поглощаемого вещества в зависимости от скорости жидкости и концентрации активной части поглотителя. Показано, что величина удельной поверхности контакта фаз при микробарботаже в 8-30 раз больше, чем при обычном барботаже, что приводит к существенному уменьшению рабочего объема аппарата при одинаковой эффективности. Сравнение с мембранными половолоконными контакторами показывает, что при использовании микропористых керамических мембран величина удельного межфазного потока в микробарботажном аппарате сопоставима или выше, чем в половолоконном контакторе.

Introduction

Currently, Kazakhstan has enormous potential for a development of agriculture, vast territories allows that country to become a leading country, both in livestock and in crops production. In order to achieve that goal, it is necessary to implement the most advanced technologies and innovations in a field of biogas implementation for energy needs by means of processing livestock wastes in biogas equipment, as a result the following products can be obtained: biogas, mineralized nitrogen fertilizer, methane, carbon dioxide, electricity, heat energy.

Biological processing is not something novel nowadays [1]. This method essentially consists of anaerobic expansion of organic wastes. Biogas, obtained by anaerobic decomposition of wastes, contains methane (\approx 60%(vol.)) and carbon dioxide (\approx 40%(vol.)). The gas contains hydrogen sulphide, ammonia, water vapor; its calorific value is quite low – 19.5-19.8 MJ/m³. After purification and drying, gas must contain not less than 98 % (vol.) of CH₄ (calorific value is not less than 33.0 MJ/m³), a concentration of N₂S should not exceed (3-5) 10^{-4} % (3-5 million⁻¹). Separation of components and production of highly concentrated methane is a big problem, which is still not solved [2].

Recently, scientific community of developed countries of the West [3], Japan [4] produced a number of publications, reporting that during a dispersion of a gas through porous membranes microbubbles are formed [5] with dimensions of $0.5-150~\mu m$. As a result of such small sizes, microbubbles have a number of unique properties, such as increased contact surface of interacting phases, they can be widely applied in chemical [6], food and pharmaceutical [7] industries, as well as in biotechnology, medicine and unconventional energy production.

As can be seen from the presented review, study of gas purification with a formation of microbubles is currently still cannot be considered complete, as an integrated approach, i.e. physical simulation, as well as design of gas separating equipment, which provides formation of microbubles and its use for purification of biogas from carbon dioxide emissions with an aim to increase methane concentration, is expected to provide new and important results in that field.

The development of technology, which allows to increase concentration of methane through a development of interphase surface, using unique microbubles properties during fine dispersion of gases, will lead to an entirely new high-efficient equipment of gas-liquid contact type, including new types of reactors and fermenter. At the same time, a preparation of biogas using a the developed microbubling equipment can provide a significant economic effect, as compared to traditional methods, for example, absorption and adsorption. The are several variants of process organization, for each of which defined parameters are required surface of membranes, cost of compression, degree of methane extraction from original mixture in different conditions. As a result of separation concentration of methane in fuel gas reaches 98% (vol.).

Due to ultra small size of generated microbubes, microbubling membrane process can be used as a basis for a development of a highly efficient biogas purification technology. In the same time, it is possible that there are no disadvantages related to limiting of loads by gas and liquid for such a technology. Unique properties of microbubles during fine dispersion of gases allows to implement that technology also in oil and gas and mining industries for a purification of associated gas and mining gas, as well as in fields of biotechnology and pharmaceutics.

Methodology

At the first stage of anaerobic half-fermenting of organic substances by means of biochemical decomposition (hydrolysis), first, decomposition of high-molecular compounds (carbohydrates, fats and proteic substances) into low-molecular compounds takes place [1,2]. At the second stage, with acid-forming bacteria taking part in the process, further decomposition with a formation of organic acids and their salts occurs, as well as spirits, CO₂ and H₂, then H₂S and NH₃. Final bacterial transformation of organic substances in CO₂ and CH₄ is carried out at the third stage of the process (methane fermentation). In addition, additional amount of CO₂ and CH₄ is formed in further from CO₂ and H₂. Those reaction occur simultaneously, at that, methane -forming bacteria form a significantly higher requirements for existence condition, as compared to acid-forming bacteria. For example, they require absolutely anaerobic media and longer time for reproduction. Speed and scaled of anaerobic fermentation of methane-forming bacteria depend on their metabolic activity.

For the study of interphase mass transfer during chemisorption of carbon dioxide by CaOH solution in membrane contactor, the method proposed by Sharma and Danckwerts was selected [8].

Distribution coefficient m was defined on a basis of experimental data on solubility of carbon dioxide in solutions of CaOH, presented in [9]. In experiments on membrane with average pore diameter of 0.5 μ m, in a case of alkali concentrations of 0.030-0.070 kmole/m³, value of m=10.3 was used, in experiments on membrane with average pore diameter of 2.6 μ m, in a case of alkali concentrations of 0.014-0.030 kmole/m³, value of m=9.9 was used,

Results of experimental studies

From the point of view of interphase mass transfer, the objects of the study were realtionships of interphase molar flow of absorbed substance, mass transfer coefficients in gas and liquid media, as well as specific interphase surface area from speed of liquid in membrane module and from concentration of active part of absorbent. The goal of the experiments was data for an estimation of effectiveness of interphase mass transfer in membrane microbubling contactor and its comparison with mass transfer equipment of other types.

For study of mechanisms of gas-liquid reaction in a case of microbubling the process of carbon dioxide chemisorption by CaOH solutions of various concentrations was selected. Because of small content of surfactants, physical properties of liquid phase (viscosity, density) were accepted the same as for clean water. Carbon dioxide and biogas mixture with CO₂ content of 10-40 % (vol.) was used in all experiments as gas phase. Studies were carried out with microporous membranes with internal selective layer and average pore diameter of 0.5 µm and 2.6 µm. For the membrane with 0.5 µm pores gas consumption (depending on liquid consumption) was 26.5-101.4 l/h (which was corresponding to pressure of 0.062-0.064 MPa), for the membrane with 2.6 µm pores gas consumption was 25.8-100.7 l/h (which was corresponding to pressure of 0.062-0.064 MPa). As liquid phase CaOH solutions with the following concentrations were used: 0.030; 0.040; 0.050; 0.060; 0.070 kmole/m³ (for the memebrane with $d_0 = 0.5$ μ m) and 0.010; 0.014; 0.018; 0.024; 0.030 kmole/m³ (for membrane with d_0 = 2.6 μ m). Those alkali concentrations were selected on the condition that, from one point of view to provide sufficient effectiveness of chemical reaction, from another point of view - to ensure necessary sensitivity for measuring equipment. Consumptions of liquid during experiments were changing in range 77-300 l/h, which corresponds to speeds of 0.7-3.0 m/s. Definition of a volume of consumed CO₂ was carried out by means of measuring of final concentration of alkali in the solution, which was coming out of module, by means of electronic device for measuring of pH.

In order to carry out microbubling process memrbrane chemisorption device is designed (figure 1), which uses membrane module made of ceramics. It consists of steel cylinder-shaped hull with 750 mm length and Ø50×3 mm diameter, inside the hull tubular ceramic membrane is installed. Direct contact between gas and liquid phases occurs in membrane module, which results in formation of fine dispersion of bubbles. Gas phase (mixture of CH₄ from CO₂ and H₂S) is fed with a required pressure inside the body from inside of membrane. Liquid phase is coming inside in ceramic membrane.

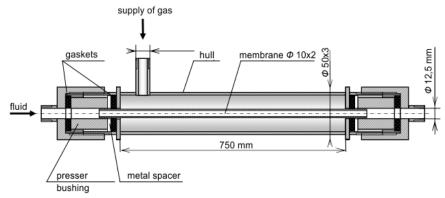


Figure 1 – Membrane module for microbubling purification of biogas from CO₂.

The experimental device consists of chemasorber (1) for carrying out of microbubbling process, vat (2), vortex pump (3) of first level of fire safety, closing (4,5,6,7,8) and regulating (9,10) valves, measuring

and control devices (Figure 2).

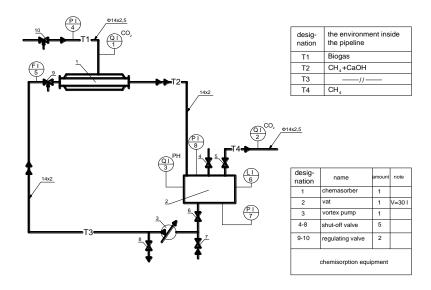
Gas mixture containing methane, CO₂, H₂S and other impurities is coming to the zone between tubes of chemasorber (1) through pipeline (T1), it is coming inside of pores of tubular ceramic microfiltering membrane and is coming out into the internal zone in a form of microbubles. Formed microbubles are continuously washed out by flow of water suspension of CaO, containing microbubles. In further, suspension together with bubbles returned to the vat (2) by means of vortex pump (3) with the following parameters: flow 0.001 m³/s, manometric head 16 mm of water column, rotation speed 24.15 rotations/s. The selected pump is of explosion-proof version.

CaO content in the suspension is 10-20% (mass). Content of CO_2 in gas mix is measured in input (QI,1) and output (QI,2) by device for measuring gas concentration pH of media (QI,3, pH) is measured in the vat (2). Pressure is measured at input of gas into the chemasorber (1) by manometer (PI,4). Flow of suspension in at input of chemasorber (1) by means of rotameter (FI,5). Volumetric flow of the suspension with bubbles is $0.5 \div 1 \text{ l/s}$.

CaO, which is contained in suspension, before complete transformation into carbonate can purify 0.8 m³ of gas mixture, containing 50% (vol/) of CO₂.

In the vat (2) level of suspension is also measured by water-gauge glass (LI,6), bottom pressure is measured by manometer (PI,7), pressure above gas-liquid layer is also measured (PI,8).

Filling of the vat (2) is carried out through valve (7) by the pump (3) with closed valves (5,6,8,10).



 $Figure\ 2-Process\ flow\ diagram\ of\ microbubling\ purification\ from\ CO_2\ of\ gas\ mixture\ containing\ CH_4.$

For emptying of the vat (2) from used suspension the pump is used (3) with open valves (6,8) and not fully closed valve (10), other valves are closed.

The room where the device is operated there is an instrument for a measurement of CH₄ concentration with alarming, when critical concentration is reached.

As a results of experiments for study of interphase mass transfer, relationships between specific interphase surface area in the device and mass transfer coefficient in gas phase and speed of liquid in channel of membrane, also value of interphase flow of absorbed substances depending on speed of liquid and concentration of active part of absorber is defined.

Figure 3 presents relationship between specific interphase surface area and speed of liquid for both used membrane. In the both cases the value of specific interphase surface is increasing with increase of speed up to values of ω approximately 2 m/s. Further increase of speed of liquid up to 3 m/s doesn't lead to a signifficant increase of interphase surface. As for value of a itself, for membranes with average pore

diameter of 0.5 μ m it is in a range of 18000-30000 m⁻¹, for average pore diameter of 2.6 μ m it is in a range of 7700-19200m⁻¹.

An increase of specific interphase surface with an increase of speed of liquid can be explained by means of features of hydromechanics of microbubling process, in particular, decrease of sizes of moving microbubbles, because of increase of resistance stress of incoming flow of liquid during their growth. At the same time, because size of formed microbubbles depedns on sizes of pores of membranes, than for membrane with $d_0 = 0.5 \mu m$ specific interphase surface is bigger then for a membrane with $d_0 = 2.6 \mu m$.

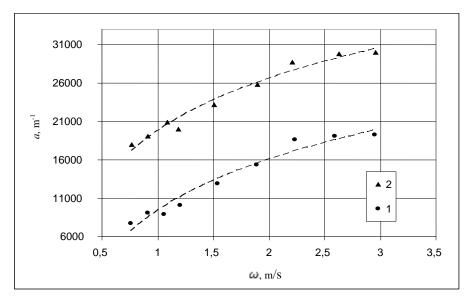


Figure 3 – Relationship of specific surface of phase contact for CO2 and speed of liquid. 1) membrane with $d_0 = 2.6 \mu m$; 2) membrane with $d_0 = 0.5 \mu m$.

Relationship between interphase flow of carbond dioxide (kmole/s) from speed of liquid is presented in figure 4. From the figure it can be seen, that for both used membranes in all cases there is virtually linear increase of value M in the studied range of speeds (0.5-3 m/s). According to the obtained data, for a membrane with d_0 =0.5 μ m during chemisorption by alkali solution with 0.07 kmole/m³ concentration M increases from $20 \cdot 10^{-8}$ to $70 \cdot 10^{-8}$ kmole/s; for a membrane with d_0 =2.6 μ m mass flow is also increase with an increase of speed, however, both M and speed of its increase are less as compared to the previous case: from $5 \cdot 10^{-8}$ to $20 \cdot 10^{-8}$ kmole/s during chemisorption by alkali solution with 0.07 kmole/m³ (figure 4). Because in a case of chemisorption with significantly fast chemical reaction hydrodynamics of bottom layers of liquid doesn't seriously influence mass transfer coefficient in liquid phase, an increase of interphase flow with an increase of speed, presumably, is caused by two factors: first, increase of specific interphase surface, second, an increase of mass transfer coefficient in gas phase.

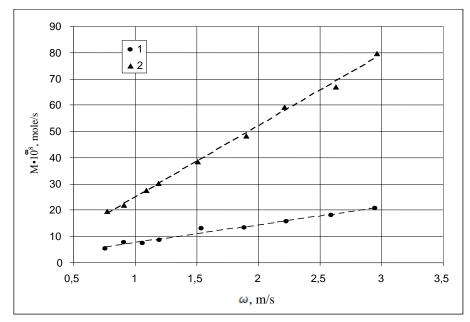


Figure 4 – Relationship of interphase flow and speed of liquid. 1) membrane with $d_0 = 2.6 \ \mu m \ (C_B = 0.03 \ kmole/m^3)$; 2) membrane with $d_0 = 0.5 \ \mu m \ (C_B = 0.07 \ kmole/m^3)$.

Let's discuss relationships of interphase flow of carbon dioxide from alkali concentration. With known values of a and k_v interphase flow can be described as follows:

$$M = \left(\frac{1}{k_y} + \frac{m}{a\sqrt{k_2 C_B D_{CO_2}}}\right)^{-1} C_{0,G} V_{work}. \tag{1}$$

In all cases interphase flow is increasing with an increase of concentration, which can be explained by an increase of mass transfer coefficient in liquid phase, which is calculated using the expression (1). Error in a description of experimental data is in a range 5-20%. Also, it can be seen, that experimental data, obtained with a membrane with pore sizes of 0.5 μ m conform to the expression (26) better, then data for a membrane with pores of 2.6 μ m size. Presumably, it is explained by higher error of the method in the second case, as in experiments with a membrane with $d_0 = 2.6 \mu$ m alkali solutions of lower concentration were used (lower alkali concentrations were selected in order to ensure necessary sensitivity of measuring instruments, because for that membrane due to lower pressure volumetric concentration of CO_2 in incoming gas mixture is lower).

The fact that obtained experimental data is in good agreement with the expression (1) may be a good indirect proof of correctness of use of the selected methodology for mass transfer studies.

Analysis of adequacy of the obtained data

Further, let's compare membrane microbubbling contactor with other types of devices.

From the results of conducted experiments it follows, that contact surface in membrane microbubbling devices depends on membrane characteristics, speed of liquid, gas consumption and, in our case, was in a range from 8000 m⁻¹ to 30000 m⁻¹.

Calculations of mass-transfer coefficient, which were carried out on a basis of experimental data, shows, that for conditions, studied in the presented paper, mass-transfer coefficient in membrane contactor (calculated for gas phase) has values of $1.6 \cdot 10^{-5} - 4.5 \cdot 10^{-5}$ m/s for a membrane with 0.5 µm pores and $2.3 \cdot 1^{-5} - 4.5 \cdot 10^{-5}$ for a membrane with 2.6 µm pores. Mass transfer coefficients in plate-type device, calculated on a condition of equal k_x' and value $k_y = 1 \cdot 10^{-3}$ m/s are $4.6 \cdot 10^{-5} - 7.5 \cdot 10^{-5}$ m/s and $2.9 \cdot 10^{-5} - 5.1 \cdot 10^{-5}$ m/s respectively. Therefore, mass transfer coefficients in plate-type device in the discussed conditions will be 1.1-2.9 times higher than in membrane contactor.

Transformation of expression (1) gives the following:

$$M = \left(\frac{1}{k_y} + \frac{m}{\sqrt{k_2 C_B D_{CO_2}}}\right)^{-1} a C_{0,G} V_{work} = k_y a C_{0,G} V_{work}, \tag{2}$$

it can be concluded, that because value of k_y membrane device is in average 1.5 times smaller and specific interphase surface is in 8-30 times higher, than in a case of the same working volumes amount of absorbed substances will increase in 5-20 times. It allows to conclude that in order to reach the desired level of absorption, membrane microbubbling device must have 5-20 smaller working volume than plate type device. At that, the following recommendations can be given. Mass transfer coefficient obtained during experiments with both membranes are quite close, but in the same time values of specific interphase surface for a membrane with d_0 =0.5 μ m are in 2-2.5 times bigger. Thus, it can be presumed, that implementation of microfiltering membranes with pores less than 1 µm will give more significant effect in decreasing sizes of a devices and, consequently, will reduce capital spendings. At that, the most optimal range of speeds of liquid, both from point of view of mass transfer coefficients and specific interphase surface is a range 1.5-2.5 m/s. At the same time, in a case of use of membrane with 0.5 μm pores necessary gas pressure is three times higher, as compared to a membrane with 2.6 µm pores. It can lead to significant energy expenses for gas blow off, especially with their expenses. Thus, for design of membrane device for a specific process technical and economic analysis should be carried out in order to find a compromise decision between a selection of type of membranes with smaller pores to reduce sizes of device from one side, and a selection of membranes with bigger pore to reduce necessary pressure from another side.

Use of membrane devices in a process of purification of biological methane from CO₂ is extensively studied nowadays [3,9,10]. Generally those are devices on a basis of hollow fiber membranes, comprising porous polymer fibers. Absorption in that kind of devices is carried out due to contact of gas through pores with liquid, flowing inside fibers, in a case there is no bubbling, pores are filled with gas (if membrane surface can't been wet) or with liquid (if membrane can be wet) and contact surface in that case depends on a number of fibers and porosity of membrane. Main advantages of that devices are small sizes, high selectivity of operation and absence of operational restrictions, which are characteristic for plate-type cap-type devices. That's a comparison of membrane contactors with hollow fiber membranes and microbubbling device from a point of effectiveness of interphase mass transfer is of a big interest.

Calculations of mass-transfer coefficient, which were carried out on a basis of experimental data, shows, that for conditions, studied in the presented paper, mass-transfer coefficient in membrane contactor (calculated for gas phase) has values of $1.6 \cdot 10^{-5} - 4.5 \cdot 10^{-5}$ m/s for a membrane with 0 µm pores and $2 \cdot 3^{-5} - 4.5 \cdot 10^{-5}$ for a membrane with 2.6 µm pores.

The figure 5 shows experimental data on specific interphase flow of CO_2 in microbubbling device and in membrane contactor with polymer hollow fiber membranes with comparable conditions. As it can be seen from the figure, in a case of use of membranes with a diameter $2.6 \mu m$ has specific flow is $3.5 \cdot 10^{-4}$ $-4.8 \cdot 10^{-4}$ mole/m²·s, which is very close to the data for hollow fiber membrane $(5.6 \cdot 10^{-4} - 6.2 \cdot 10^{-4} \text{ mole/m}^2 \cdot \text{s})$. In the case with the membrane with $0.5 \mu m$ pores specific flow varies from $5.6 \cdot 10^{-4}$ to $11.3 \cdot 10^{-4} \text{mole/m}^2 \cdot \text{s}$ and exceeds values for hollow fiber membrane, especially at speeds of liquid of $1.5 \cdot 2.5 \cdot 10^{-4} \cdot$

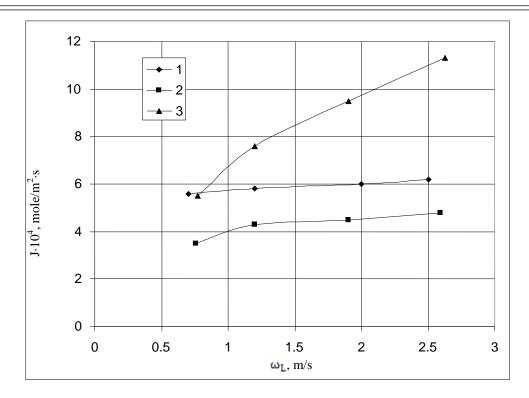


Figure 5 – Comparison between specific interphase flow in the microbubbling device and membrane contactor with hollow fiber membranes during chemisorption of CO_2 water solution of CaO ($C_B = 0.1 \text{ kmole/m}^3$).

1) Hollow fiber membrane with $d_0 = 0.2 \,\mu\text{m}$ (reference data); 2) ceramic membrane with $d_0 = 2.6 \,\mu\text{m}$; 3) ceramic membrane with $d_0 = 0.5 \,\mu\text{m}$.

Conclusion

As it was noted, all presented conclusions are based on the provisions of film model of substance's transfer. However, penetration model also can be used for a description of membrane microbubbling method. Therefore, a comparison of relationships obtained by film and penetrations model is of big interest. Existing theories regarding chemisorption, even though they can't be considered complete, provide sufficiently reliable results for a case of fast nonreversible reactions of first and pseudo-first order. At the same time, in fact, all models of mass transfer are demonstrating similar values for mass transfer coefficient for chemisorption.

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Жоғарыконцентрациялы метанды алу мақсатында биогазды тазалаудың энергоүнемдеу технологиясын тәжірибелік зерттеудің нәтижелері

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Түйін сөздер: Биогаз, микробарботажды аппарат, түтікшелі керамикалық мембрана, жоғарыконцентрациялы метан, дәстүрлі емес энергетика, математикалық моделдеу, массаалмасу, сұйық, газ, микробарботаж.

Аннотация. Фазаааралық массаалмасу тұрғысынан қарағанда зерттеу нысаны ретінде сіңірілуші заттың фазааралық мольдік ағынының, газ және сұйық фазалардағы массаалмасу коэффициенттерінің, сондай-ақ фазалардың әрекеттелуші меншікті бутінің мембраналық модульдегі сұйық жылдамдығына және сіңірушінің белсенді бөлігінің меншікті концентрациясына тәуелділігі алынды. Тәжірибе мақсаты, бұл мембраналы микробарботажды контактордағы фазаларының массаалмасудың тиімділігін бағалау үшін мәлімет алу және оны басқа типтегі массаалмасу аппараттарыменен салыстыру.

Фазааралық массаалмасуды зерттеу бойынша зерттеулер нәтижесінде аппараттағы меншікті фазааралық беттің және мембрана арнасындағы сұйық жылдамдығының газ фазасындағы массаалмасу кэффициенті, сондай-ақ сіңіруші

заттың фазааралық ағыс шамасының сұйық жылдамдығына және сіңіргіштің белсенді бөлігінің концентрациясына тәуелділігі анықталды. Микробарботаждағы меншікті фазаның жанасу беті жай барботажға қарағанда 8-30 есе үлкен екені көрсетті, бұл бірдей тиімділікте аппараттың жұмыс көлемін едауір кемитуге алып келеді. Мембраналы кұысталшықты контактормен салыстырғанда, құысталшықтыға қарағанда микрокұысты керамикалық мембраналарды қолданғанда микробарботаждық аппараттың меншікті фазааралық ағыны сәйкес немесе жоғары екенін көрсетті.

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