Intensification of mass transfer processes using membrane contactors based on nanoporous membranes

The purification of natural and associated petroleum gases from sulfur-containing and "acidic" components such as H_2S, CO_2, mercaptans, and gas dehydration are crucial challenges in the oil and gas industry, both in Russia and internationally. Current methods, including refrigeration, adsorption, and absorption techniques, have limitations such as high energy consumption and bulky mass transfer equipment, restricting their applicability, especially in small fields. Membrane technologies have emerged as a promising alternative, leveraging selective permeation of gas components through membranes without the need for energy-intensive heating or cooling. However, existing membranes lack the required selectivity, especially for deep purification tasks, leading to significant losses of target components.

This study explores hybrid gas treatment technologies employing membrane contactors, specifically a method known as pertraction (permeation + extraction), where liquid absorbents remove contaminants through a membrane. To optimize gas-liquid contact, non-porous high-performance selective layers or porous materials with nanoscale channels are utilized. These innovative approaches, involving materials like graphene and transition metal oxides, enable efficient gas separation, preventing wetting of the membrane surface and ensuring gas-phase transport. Hybrid technologies offer advantages over traditional methods, such as compact setups, reduced absorbent volume, spatial separation of gas and liquid phases, independent flow control, and prevention of channeling and foaming. Gas-liquid contactors prove highly effective in various gas separation processes, providing a versatile solution for extracting different components based on the chosen liquid absorbent.

This work focuses on the development of novel nanoporous membrane materials and processes for the extraction of components from gas mixtures, specifically for the purification and dehydration of natural and industrial gases.

The study investigates the efficiency of gas and vapor interphase transport through nanoporous membranes in a liquid absorbent solution. Key patterns in the selective removal of gas mixture components in membrane contactors are established. Parameters such as the content of the removable component in the feed stream, the saturation level of the liquid absorbent, feed and absorbent flows, process pressure, and interphase pressure drop were considered. The research reveals that the efficiency of membrane contactors is significantly influenced by the interphase pressure drop, determining the diffusion regime of the removable component through the membrane pores, and the diffusion of extracted components (or products) into the liquid absorbent layer.

Reducing the chemical potential of the removable components in the sub-membrane space, while keeping the chemical potentials of other gas mixture components equal, significantly reduces losses in the prepared gas and ensures high process efficiency due to the high permeability of the porous membrane. The study utilizes a developed mathematical mass transfer model in gas-liquid membrane contactors, considering system geometry, flow velocity distribution, diffusion of components in gas and liquid phases, pore diffusion, absorption of components by the liquid absorbent at the gas/liquid interface, and chemical equilibria in the liquid absorbent. The model explains the significant impact of the absorbent flow rate on the efficiency of membrane contactor operation. It demonstrates that pertraction performance is limited by mass transfer in the liquid absorbent phase. For CO_2, the gas absorption rate into aqueous absorbent solutions is limited by the dissociation rate constant of $CO_{2\,(aq)}$, whereas for hydrogen sulfide, no such effect is observed. This insight allows the selection of conditions for selective removal of hydrogen sulfide in the presence of carbon dioxide, reducing absorbent consumption (when using alkali) or the load on the regeneration column (when using amine solutions).

A synergistic effect, based on effective heat exchange and condensation of vapors in the cooled liquid absorbent, was discovered. This effect was utilized to create a membrane absorption-condensation contactor, using chilled monoethylene glycol solution as the working fluid. This innovation enabled the preparation of feed gas to a dew point below -30°C with water vapor extraction rates reaching 99%.

For gas mixture dehydration, ultrathin (up to 50 nm) gas-tight composite membranes based on graphene oxide layers were proposed. The study investigated the structure of selective layers in operando, revealing that water vapor transport between nanolayers depends on the interlayer distance, varying from 7.2 Å to 11.5Å depending on water partial pressures in the feed stream and permeate. Increasing the interlayer distance transitions the diffusion mechanism from a jump mechanism to a capillary condensation mechanism in the interlayer space, allowing for membrane permeability to water vapor of approximately 90,000 L(STP)/($m^2 \cdot atm \cdot h$) and H_2O/N_2 selectivity exceeding 10,000.