ABSTRACT OF THE DOCTORAL DISSERTATION "Polymeric membranes for pervaporative recovery of butanol from quaternary butanol-ethanol-acetone aqueous mixtures." Author: mgr Jan Kujawski Supervisor: prof. dr hab. inż. Marek Bryjak

The production of butanol by the fermentation method requires the use of efficient techniques for its separation from diluted aqueous solutions. Vacuum pervaporation is one of the membrane separation techniques that is used to the removal of volatile organic compounds from water. In this work, pervaporation has been used as a technique for removing volatile ABE fermentation products from model aqueous mixtures.

It must be remembered, that the membrane plays an essential role in the separation process, being responsible for transport and selective properties of the separated system.

The research was divided into several stages. First, an effective polymer was selected for the selective removal of butanol from dilute binary and multicomponent aqueous solutions. To this end, by using theoretical considerations based on Hansen solubility (HSP) parameters and Flory-Huggins interaction factor, over 500 polymer materials were screened, estimating the range of interactions with butanol, acetone, ethanol and water. Boundary conditions assuming interaction of the material with butanol and ethanol and weak interaction with acetone were used.

As a result of this screening procedure, the best 2 polymers were selected from the database: Butvar B-98 (polyvinyl butyrate copolymer containing 20% of polyvinyl alcohol) and Plastopal H (urea-aldehyde resin). Finally, Butvar B-98 was selected because of the presence of hydroxyl groups. The surface properties of formed membranes and their separation and transport properties in butanol removal from water were subsequently determined.

The analysis of the surface properties of the formed membranes enabled the determination of their thermal stability, the manner of silane compound attachment during the crosslinking process and the connection of separation properties with the dispersive part of surface free energy (SFE).

Membranes cross-linked with 3-aminopropyltrimethoxysilane were characterized by more than 20 times greater separation efficiency against butanol than acetone. Examination of the participation of crystalline membranes allows for their pre-selection prior to testing in the pervaporation process.

The properties of the formed membranes (using various crosslinkers as well as the addition of nanofillers) were compared with properties of commercial membranes tested in the next stage of work. The effectiveness of commercial PDMS membranes (Pervatech, PervapTM1060, PervapTM1070, PervapTM4060) in the pervaporation process for ABE removal from water was also determined. Among the commercial membranes tested, the PervapTM4060 membrane showed the highest value of Pervaporation Separation Index (PSI).

The formed membrane based on poly (vinyl butyrate) was characterized by a PSI value about 10-12% higher than in the case of commercial membranes for a system containing 1% butanol in the feed. Moreover, this membrane was characterized by a separation factor for acetone $\beta < 2$.

The use of HSP and χ parameters enabled the design of membranes with pre-assumed properties.

This dissertation is one of the few in which Hansen's solubility parameters and the Flory-Huggins interaction coefficient are used as a method of selecting of the polymeric material for forming membranes with pre-assumed properties. It is also one of the first works in which the separation properties of membranes formed on the basis of polyvinyl butyrate in contact with model aqueous solutions of acetone, butanol and ethanol were examined.