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MEMBRANE PROCESS DESIGNS IN THE RECOVERY OF BIO-FUELS AND BIO-CHEMICALS

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In this presentation, the emerging membrane unit operations and process designs that can be used in recovery of fuels and organic chemicals produced via bioconversion are briefly summarized. Product recovery costs are a major barrier to increased use of bioconversion for the production of fuels and chemicals. The integration of developing membrane unit operations into product recovery schemes may reduce process energy requirements and costs. This presentation is based primarily on two extensive reviews (Leeper, 1986;1990).

Membrane unit operations that are used or studied in recovery of bio-fuels and organic chemicals include pervaporation (PV), vapor permeation (VPe), reverse osmosis (RO), membrane extraction, and electrodialysis (ED). Although it can be argued that ultrafiltration (UF) is used to purify bio-fuels and bio-chemicals, UF is not included in this survey for two reasons: 1.) the primary uses of UF in bioprocessing are to clarify fermentation broth and to retain cells/enzymes in bioreactors and 2.) the literature on UF in biotechnology is expansive. Products of bioconversion for which data are compiled include ethanol, acetone, butanol, glycerol, isopropanol, ethyl acetate, fusel oils, acetaldehyde, acetic acid, butyric acid, citric acid, propionic acid, succinic acid, and tartaric acid.

<u>Developments in Product Dehydration</u>: PV is being used to dehydrate ethanol and other organic chemicals. VPe is being studied and could be a viable approach. RO has been considered (in theory only) for dehydration of ethanol; however, appropriate RO membranes are not presently available (Leeper and Tsao, 1987).

The use of PV to dehydrate ethanol, isopropanol, and other organics is rapidly becoming established technology. Pilot and commercial plants for dehydration of ethanol, isopropanol, acetone, and butanol are operating in Europe, Asia, and Japan. For ethanol processing, feedstreams containing 92 to 94 wt% ethanol are dehydrated to 99.5 to 99.95 wt% ethanol. PV produces products which are essentially anhydrous. Commercially-available PV membranes include the GFT membrane, which consists of polyvinyl alcohol on polyacrylonitrile, and the BP Kalsep membrane (proprietary material). Detailed data have been published on the performance of the GFT membrane for ethanol- and isopropanol-water mixtures. Additional materials, including cellulose acetate, polysulfone, polyacrylic acid (and its derivatives), fluorinated materials, and polyacrylonitrile, are being studied. PV has also been studied for the dehydration of acetic acid (polyacrylate membranes), ethyl acetate (silicon rubber and polyvinyl alcohol membranes), and fusel oils. Dehydration of multicomponent mixtures should be possible. Additional reviews on organic chemicals dehydration by PV include Frennesson et al (1986), Sander and Soukup (1988a), and Bruschke (1988; 1990).

VPe is emerging as a promising candidate for dehydration of organic chemicals. The feed stream to VPe is a vapor; therefore, VPe fits well with fractional distillation (since only partial condensation of the distillate is required). VPe pilot plants for ethanol and isopropanol dehydration are

reportedly being built. Candidate membranes include cellulose acetate, polyamide, and proprietary materials. The separation factors obtained with VPe membranes can be extremely high (>100), with flux equivalent to (or slightly lower than) PV. VPe technology is also reviewed by Meares (1988) and Sander and Soukup (1988b).

Developments in Organics Recovery from Dilute Solution: PV, RO, ED, and membrane extraction are being studied for recovery of ethanol, acetone, butanol, and isopropanol from dilute solutions (e.g., fermentation broths). These operations may be useful for partial concentration of organics, prior to further concentration by fractional distillation. The feasibility of these applications requires performance breakthroughs.

Various PV materials, including silicon rubber (polydimethylsiloxane), silicon rubber derivatives, fluorinated polymers, and polyethylene, have been studied. For ethanol recovery, silicon rubber PV membranes exhibit low flux (up to 0.7 $kg/m^2/h$) and moderate separation factors (up to ~12). Polytetrafluoroethylene/polypropylene membranes may be a promising material. Several studies have demonstrated that productivity of product-inhibited fermentations can be increased using PV to continuously remove products. Membrane performance is generally lower when the feedstream is a fermentation broth (as compared to aqueous solutions). This use of PV has also been reviewed by Bitter (1988).

RO may be useful for partial concentration of organic chemicals at low concentration (Leeper and Tsao, 1987). For ethanol recovery, high flux (up to 20 $kg/m^2/h$) and reasonable rejection (50 to 99+%) are exhibited by several membranes. The best performance occurs at low ethanol concentrations. Extremely high flux and rejection have been reported for low (~1 wt%) isopropanol concentrations (PEC-1000 and NS-100 membranes). Encouraging performance data are reported for acetone, butanol, acetic acid, and butyric acid using polyamide membranes. The polybenzimidazolone (PBIL) membrane exhibits high rejections for citric acid, glycerol, succinic acid, and tartaric acid and moderate rejections for acetaldehyde and propionic acid.

ED bioreactors are being studied for the production of lactic and acetic acids. Removal of lactic acid reportedly improves productivity three- to four-fold (Rosenau et al, 1986). For acetic acid fermentation, a productivity improvement of 35% was reported (Nomura et al, 1988).

Membrane extraction (Matsumura and Markl, 1984) has been investigated for ethanol recovery from fermentation broth. This approach can eliminate solvent toxicity problems, frequently encountered in continuous fermentation/extraction processes for recovery of ethanol from fermentation broth.

Conclusions: Interest in membrane operations for the recovery of bio-fuels and bio-chemicals is increasing dramatically. Membrane processes are emerging and are becoming viable candidate operations for integration into product recovery systems. Maximum advantage can be taken of the capabilities of membranes when membrane operations are used in hybrid systems with other separation technologies.

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