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THE FEASIBILITY OF PERVAPORATION IN THE PURIFICATION OF ETHANOL

A thesis presented in partial fulfilment of the requirements for the degree of Doctor
of Philosophy in Process and Environmental Technology at Massey University.

Lilian de Barros Ferreira

1998

All animals, except man, know that the principal business of life is to enjoy it.

S. Butler.

ABSTRACT

This study investigated how pervaporation could be incorporated into hybrid schemes for purifying ethanol produced from whey of fusel oils and whether this could be achieved at a lower energy cost than distillation alone whilst maintaining product quality within specification. In order to achieve these objectives the project included: investigation of fundamental pervaporation mechanisms and the influence of operation parameters, simulation of the distillation train at the New Zealand Distillery Co. Ltd. (NZDCL) including pervaporation relationships developed during this study, and pinch analysis of the NZDCL.

Aqueous solutions of 5 to 20% w/w ethanol with approximately 1% w/w of a mixture of *n*-propanol, *i*-butanol, *n*-butanol, *i*-amyl alcohol and ethyl acetate were pervaporated through a disk apparatus fitted with either poly-ether-block-amide (PEBA) or poly(dimethyl siloxane) membranes. Similar solutions were sorbed into PEBA beads for the study of sorption.

A new, semi-empirical relationship between enrichment factor of alcohols during pervaporation and their molecular size and activity coefficient in the feed stream was proposed. It was observed that for organophilic membranes, sorption generally sets the enrichment factor while the influence of diffusion becomes relevant only when the distribution range of the size of the molecules involved is quite large. In consequence, it is recommended that the study of sorption and diffusion relationships between solvents and dense polymers be given priority as they are relevant for the fast development of this technology.

During pervaporation, the temperature of the feed affected mainly the process economics, as an increase in temperature resulted in an exponential increase in the total flux, without significantly changing the product composition.

The flux of the minor components studied was independent of the total flux through the membrane except for the *i*-amyl alcohol, which had its flux influenced by the total flux possibly due to its higher concentration.

For the removal of fusels from the fermentation broth with organophilic membranes, all three commercially available membranes investigated presented similar enrichment factors and, compared to evaporation, did not significantly improve the separation of fusels from ethanol. The membranes investigated differed amongst each other with respect to their total flux; the higher the flux through the membrane, the lower the membrane area required for a specific separation.

Hydrophilic membranes were used to remove the water fraction at an earlier stage of distillation. Simulation and experiments of the new process showed that it was possible to reduce design complexity and energy expenditure by approximately ten percent. This process could become economically feasible if membrane price dropped by over 60%.

Pinch analysis and simulation results of distillation were combined to investigate immediate opportunities to reduce energy usage at NZDCL. Changes in the heat exchanger network and in the distillation feed temperature could reduce production costs (steam usage) without compromising product quality and plant flexibility.

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