CHAPTER II

LITERATURE REVIEW

2.1 Pervaporative Membrane Reactor

The majority of published researches on membrane reactors to date are in the field of biotechnology. The membranes used are typically micro-porous, and the functions of membranes are mainly for immobilizing enzymes, eliminating product inhibition, recycling enzymes and other biocatalysts, and manipulating substrates and nutrients. Recently, the extensive studies have been focused on membrane reactors applied to catalytic dehydrogenation, hydrogenation, and decomposition reactions. However, the minority of works have been done on liquid-phase reversible reactions due to lack of suitable membranes with good permselectivities and solvents resistance. Ultra-filtration membranes are too porous to effect the efficient separations of small liquid molecules, while reverse osmosis membranes require an inconveniently high operation pressure due to the osmotic pressure of reaction mixtures. An emerging pervaporation membrane process specially used for organic-water and organic-organic separations seems to be an appropriate choice (Feng and Huang, 1996). In this process, the mass transports through the membrane are induced by maintaining a low vapor pressure on the downstream side, thereby eliminating the effects of osmotic pressure.

A concept of using pervaporations is to remove by-product species from reactions. Recently, pervaporations are best applied for the dehydration of organic solvents, and the dehydration membranes normally work best when water contents in feed mixtures are not high. Thus, reversible reactions which produce by-product, water, are a niche of pervaporation for reactions enhancement.

Etherification represented a significant group of the reactions commonly found in the chemical industry. The uses of pervaporative membrane reactor for etherifications are different from that of reactive distillations in which water is externally removed at the top or bottom stream. In the pervaporative membrane reactors, the by-product, water, is simultaneously removed from the reaction region while the reaction occurred.

A pervaporation-based hybrid process was analyzed by (Okamoto et al., 1993) for the esterification of oleic acid with ethanol using *p*-toluene sulphonic acid as a catalyst to produce ethyl oleate. The reaction was carried out within the pervaporation unit using a process layout similar to the membrane reactor with asymmetric hydrophilic poly-etherimide (PEI), and 4,4'-oxydiphenylene pyromellitimide (POPMI) membranes. Through the application of this hybrid process, a 98% conversion was achieved in experiments.

There were a number of works on developing new processes to improve the etherification yield. (Matouq et al., 1994) proposed a process layout combining an external pervaporation process using hydrophilic polyvinyl alcohol (PVA) membranes with reactive distillation for the production of MTBE. Two types of catalysts, ion exchange resin Amberlyst 15 and heteropoly acid (HPA) for the reaction of methanol and TBA to produce MTBE, were investigated. HPA showed a higher selectivity than ion exchange resin. It was found that the hybrid process using pervaporation might be effective for water removal.

(Yang and Goto, 1997) have implemented the similar process for the production of ETBE from EtOH and TBA using Amberlyst 15 as a catalyst. Microporous hydrophilic hollow fiber membranes were employed in the pervaporation unit for the bottom product dehydration in the reactive distillation column. Shifting the reaction equilibrium led to almost doubling of the ETBE product mole fraction in the top product.

(Worapon, 2001) has investigated a pervaporative membrane reactor for the synthesis of ethyl *tert*-butyl ether (ETBE) from a liquid phase reaction between ethanol and *tert*-butyl alcohol. The studies were divided into 3 parts: kinetic studies of supported β-zeolite, studies on permeation through polyvinyl alcohol (PVA) membrane and studies on pervaporative membrane reactor. In the pervaporative membrane reactor studies, both experiment and simulation were carried out. An activity-based model was developed to investigate the performance of the pervaporative membrane reactor using parameters obtained from the independent experiments. The simulation results agreed well with the experimental results.

(Assabamrungrat, 2003) has developed the mathematical models for a synthesis of ethyl *tert*-butyl ether (ETBE) from a liquid phase reaction between ethanol (EtOH) and *tert*-butyl alcohol (TBA) in three modes of pervaporation membrane reactors (PVMR) operation; semi-batch reactor (SBR), continuous stirred tank reactor (CSTR) and plug flow reactor (PFR). Simulation results of SBR agreed well with experimental results. The same kinetic and mass transfer parameters as in SBR were used for the CSTR and the PFR models. Modelings the synthesis of ETBE from TBA and EtOH in PVMRs demonstrate:

1. PVMRs are superior to the conventional reactors due to selective removal of H_2O from the reaction mixture.

2. PFR mode of PVMR operation is more preferable to the CSTR mode although there are some ranges of operating conditions where the CSTR mode offered higher yield but these occurred at low yields.

3. Operating temperature is a key parameter to determine the reaction selectivity. Operation of PVMRs at low temperature with a high ratio of membrane area to catalyst weight is desirable.

4. Feed ratios of EtOH and TBA at the stoichiometric value or slightly higher lead to higher ETBE yields.

2.2 Neural Network Application in Control Systems

The Majority of the neural networks utilized in these applications are multilayered feed forward networks, recurrent networks, and radial basis function networks. There is no clear advantage of one network over the other as well as of any one activation function over the other. These will be strongly dependent on the user and their applications and have to be considered in a case-by-case basis.

The applications utilizing these neural network based control strategies are widely ranged involving typical chemical process systems, from the linear to highly nonlinear systems. However, the most common systems used are the distillation columns and the reactor systems (continuous stirred tank reactors, bioreactors and the neutralizing reactors). These multivariable nonlinear systems are really suitable for testing such control algorithms in chemical process systems. Neural networks are often used in many control configurations. However, those control systems can be grouped into three control techniques, model predictive control, inverse-model-based control, and adaptive control. The methodology to implement these control techniques, how neural networks are employed in the control configurations and the neural network applications in those control configurations are proposed, respectively. The various neural network control configurations can be found in (W. T. Miller, R. S. Sutton and P. J. Werbos, 1990; D. A. White and D. A. Sofge, 1992; K. J. Hunt, D. Sbarbaro, R. Zbikowski and P. J. Gawthrop, 1992; B. Widrow, D. E. Rumelhart and M. A. Lehr, 1994; M. Brown and C. Harris, 1994; A. J. N. Van Breemen and L. P. J. Veelenturf, 1996; B. Widrow and E. Walach, 1996; S. N. Balakrishnan and R. D. Weil, 1996; M. Agarwal, 1997; T. H. Kerr, 1998; C. L. Lin and H. W. Su, 1999; S. Brückner and S. Rudolph, 2000; A. Fink, S. Töpfer and R. Isermann, 2003; E. K. Juuso, 2005), for example.