# CHAPTER II

# LITERATURE REVIEWS

## 2.1 Dilute Acetic Acid Recovery

As dilute acetic acid can be found as by-products in many chemical industries, recovery of the dilute acetic acid becomes important issues due to economic and environmental awareness. Conventional processes to recovery acetic acid from its aqueous solution normally involves with extractive distillations. By adding a third component, the volatility of water is increased and the separation can be achieved with less energy. It is noted that due to a closed boiling point of acetic acid and water, the separation of their mixture solution by using a traditional distillation is difficult, requiring the column with many stages and a high energy consumption.

Alternative processes for dilute acetic acid recovery is liquid-liquid extractions; acetic acid is extracted from water by a suitable solvent in order to obtain substantially pure acetic acid. Figure 3-1 shows the flow diagram of a conventional extraction plant for the recovery of acetic acid. It consists of the extraction tower, the rectification tower for the recovery of the extraction agent, and water-stripping tower. The bottoms product from the rectification tower contains acetic acid concentration of practically 100 wt %.

Recently, the application of reactive distillation has become a potential alternative method for the recovery of dilute acetic acid and has attached numerous research activities. Performing separation and chemical reaction in a single distillation column offers advantages not only to separate acetic acid from aqueous solution but also to produce a valuable product at the same time, thereby reducing capital and energy costs. The recovery of dilute acetic acid using a reactive distillation column was first studied by Neumann and Sasson (1984). They studied the esterification of dilute acetic acid with methanol using a chemorectification column packed with an acidic organic polymer catalyst. The detailed reaction kinetics, experimental, and

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theoretical studies were performed in the range of 20-60 wt % of acetic acid. An investigation was also made to study the rate equation of the esterification under heterogeneous catalysis, 8 % cross-linked Dowex 50W polymer. Kinetic studies showed the reaction to be an intermediate type where both diffusion and the chemical reaction were partially controlling. The process was tested both experimentally and theoretically by computer simulation. Comparing results of the simulation with the experimental results were good agreement and a substantial acetic acid conversion of 70-80 % was achieved.

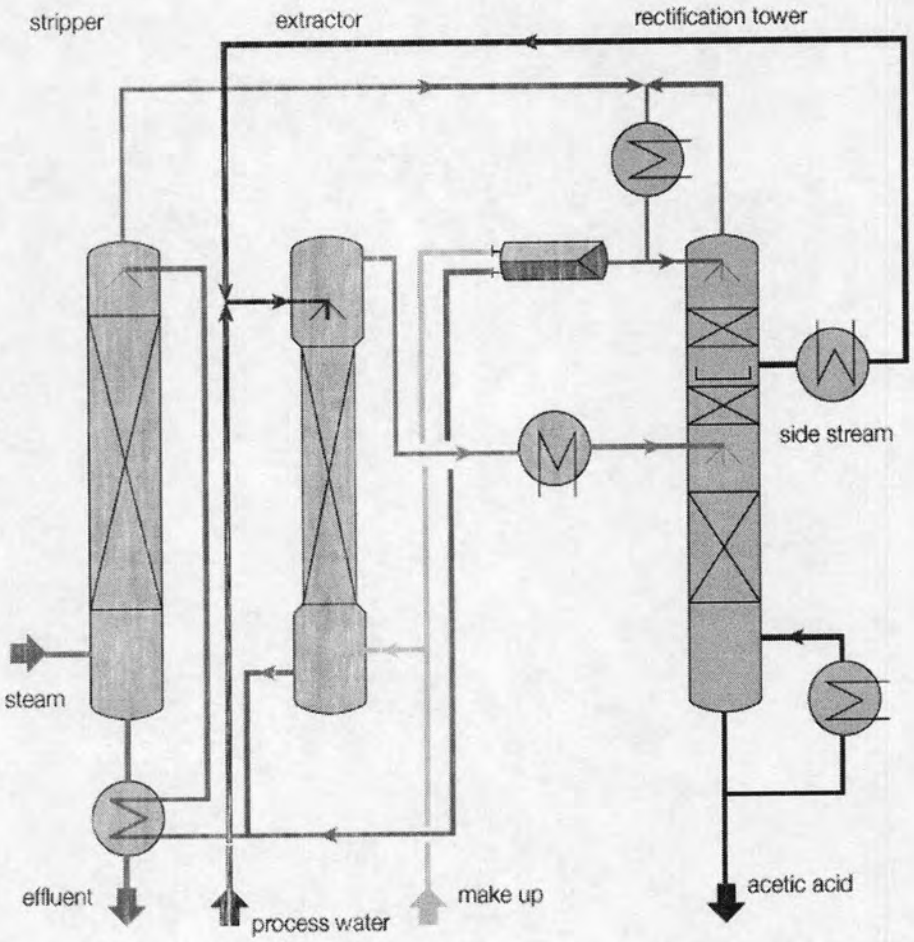


**Figure 2-1** Conventional liquid-liquid extraction for separation of acetic acid and water (QVF Process Systems Ltd.).

Xu et al., (1999) studied the separation of dilute acetic acid from water using a catalytic distillation where dilute acetic acid is reacted with methanol via esterification catalyzed by Amberlyst-15 to produce methyl acetate. For the feed that contains 2.5-10 wt % w/w of acetic acid in water, experimental results showed that the acetic acid conversion of 50 % can be obtained with roughly 30 wt % methyl acetate on the product stream.

Singh et al., (2006) examined the recovery of acetic acid solution in range of 5-30 wt % by reactive distillation through esterification with methanol in the presence of ion-exchange resin (Amberlyst-CSP2). Based on experimental result, for the feed containing 30 wt % (11.5 mol %) of acetic acid in water, more than 80 % of acetic acid recovery as methyl acetate was realized. Various alternative scenarios such as effect of reboiler duty, feed flow rate, and feed composition, were covered in the experiments. For simulation studies, the equilibrium stage model of reactive distillation consisting of the MESH equations give a good performance prediction compared with the experimental results.

Saha et al., (2000) reported experimental results on the recovery of dilute acetic acid (30 wt %) through esterification with higher alcohols such as *n*-butanol and iso-amy alcohol in a reactive distillation column using macroporous ion-exchange resin (Indion 130) as a catalyst bed. The reactions were found to be equilibrium limited. The different column configurations were studied by changing the reflux location, length of catalytic zone, and length of the total column height to get optimal results. The effect of various parameters, for example, feed flow rate, feed location, reflux ratio, molar ratio of reactant and effect of recycle of water was studied experimentally. In a typical column configuration with 1:2 mole ratio of acetic acid to n-butanol, 58 % conversion of acetic acid was achieved whereas with 1:2 mol ratio of acetic acid to iso-amyl alcohol, 51 % conversion of acetic acid was achieved. The best result was obtained when the column was operated in counter-current mode.

Bianchi et al., (2003) studied the recovery of very dilute acetic acid (6 wt %) using *n*-butanol and 2-ethyl-1-hexanol in a simple glass reactor taking advantage of the different solubilities of acetic acid and acetic ester in water. Different acid

catalysts were tested in both homogeneous (i.e., sulphuric acid 96%) and heterogeneous catalysts (i.e., Amberlist-200, Amberlist-15, Amberlist-IR120 and Nafion NR50). The esterification of 6% aqueous solution of acetic acid with alcohol is obviously a reversible reaction and the conversion is greatly restricted by equilibrium limitation. Almost 70% conversion can be obtained with 5 h of residence time. These experimental results showed the good performance of sulphuric acid as an esterification catalyst in their condition. However, all the side effects of the use of this kind of acid are well known: corrosion problems and the residual contamination of the purified water by means of the $SO_4^{2-}$ ions. For these reasons, the use of solid acid catalysts is most preferable. However, their performances are dramatically lower than the homogeneous catalysts.

Hung et al., (2006a) explored the recovery of acetic acid aqueous solution with different acid concentrations (varying from 100 wt %, 75 wt %, 50 wt % and then to 30 wt %). Instead of separating acid from water using azeotropic distillation, acetic acid is converted to acetate via esterification with various alcohols, i.e., methanol, to ethanol, to 2-propanol, to *n*-butanol, to *n*-pentanol. A total annual cost (TAC) was used as a steady-state economics criterion to discriminate different design alternatives. A preliminary screen eliminated ethanol, 2-propanol and n-butanol because of higher TAC that are observed when pure acetic acid is used. As a consequence, the esterification using methanol and amy alcohol is much more economical as compared to other choices. Then, a systematic design procedure was taken to design the process flowsheets, with and without pretreatment unit. After process design analysis was performed, it was found that methanol is less preferrable reactant because it shows either a limited ability to handle the variation of acetic acid concentration (flowsheet without pretreatment) or a expensive cost for acetic acid dehydration with a high purity acetic acid specification (flowsheet with pretreatment). In addition, the TAC analysis showed that a stand-alone reactive distillation is more economical than that with the pretreatment unit.

## 2.2 Production of Butyl Acetate by Reactive Distillation

Tranditional processes for the production of butyl acetate via esterification comprised of a pack-bed reactor connected with a distillation. Generally, butanol-acetic acid mixture (49% mol acetic acid) is fed to the reactor which is packed with strongly acidic ion exchange resin and then a reactor effluent is sent to a distillation to separate a butyl acetate product from other substances. Since esterification is equilibrium limited, the application of reactive distillation for this reaction system seems to be an attractive method and has been received much attention by many researchers.

Hinaka et al., (1999) studied the synthesis of butyl acetate using a reactive distillation column in which solid acidic catalysts are packed inside a catalytic zone. Two sets of experiments consisting of a reactive distillation column and a primary reactor connected with the reactive distillation column were performed. ASPEN PLUS software was also used for the simulation of butyl acetate synthesis. A comparison of experimental data with the simulation results showed good agreement. They also proposed a new butyl acetate manufacture technology (Figure 3-2) which is based on the pilot plant research data.

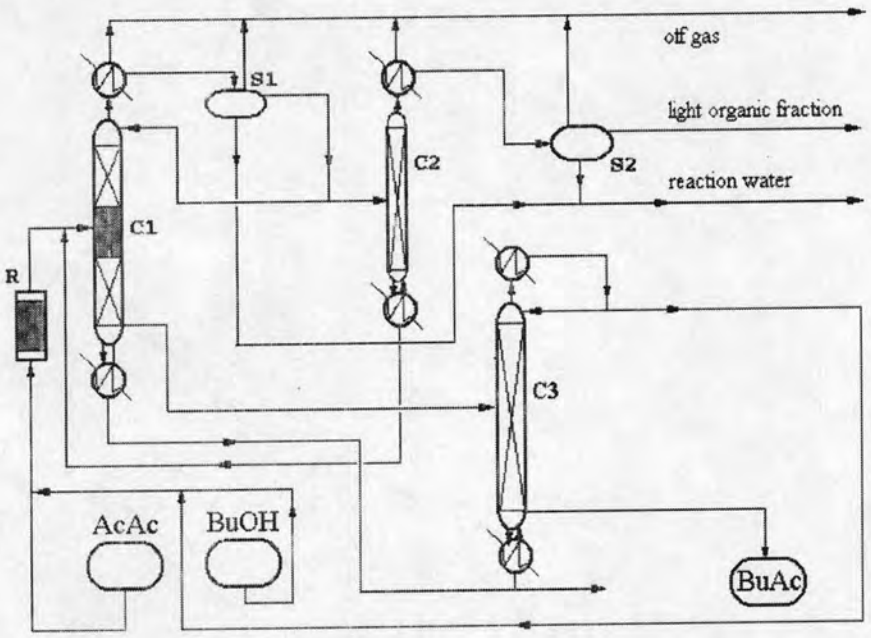


**Figure 2-2** Schematic of the new butyl acetate process (Hinaka et al., 1999).

Smejkal et al., (2002) investigated the production of butyl acetate from esterification of acetic and *n*-butanol. The pilot plant system included an equilibrium reactor and a reactive distillation column. A mixture of reaction products near its equilibrium composition (67% conversion) obtained from the equilibrium reactor is fed into the reactive distillation where the reactants are further reacted and at the same time, the butyl acetate product is separated. As the result, the conversion of *n*-butanol is increased. The results obtained from experiments were also compared with that from simulations using ASPEN PLUS and HYSYS software. In the simulation studies, the esterification was assumed at equilibrium condition ($K_{eq}$ = 4.27) and activity coefficients were calculated by NRTL method. An excellent agreement between experimental data and simulation results was observed. By comparing the results of ASPEN PLUS and HYSYS software, it was found that both programs gave similar results of the concentration profile along the column.

Steinigeweg et al., (2002) studied the influence of various operating conditions, i.e., reboiler duty, total feed flow and reactant ratio, on the performance of a reactive distillation in the production of *n*-butyl acetate. The experiment demonstrated that for an equimolar ratio of reactants *n*-Butanol conversions of 98.5 % accompanied by n-butyl acetate purities of 96.9 % were achieved. A comparison of the experiment data with the simulation result caculated by ASPEN PLUS indicated that an equilibrium stage model is capable of describing the behavior of the reactive distillation column quantitatively.

Another work focusing on the production of butyl acetate by a reactive distillation was carried out by Gangadwala et al., (2004). An equilibrium stage model based on the intrinsic kinetics of the esterification and the unwanted side-reaction etherification over the Amberlyst-15 catalyst was developed and validated with experiment data reported in literature. With the proposed model, three different configurations of the reactive distillation column are investigated with regard to the impact of important design variables on the column performance. . It was found that the column with a reactive section and nonreactive stripping and rectifying sections is most suitable and optimum values of various design parameters such as reboiler duty,

catalyst loading, catalyst section length and location, and feed tray location were determined.

## 2.3 Control of Reactive Distillation Column

Al-Arfaj & Luyben (2000) explored the closed-loop controls a reactive distillation column in which two products are produced in a single column and stoichiometric amounts of fresh feeds are desired. The reversible reaction is $A + B \Leftrightarrow C + D$. The relative volatilities are favorable for reactive distillation; i.e., the reactants are intermediate boilers between the light product C and the heavy product D. Simple ideal physical properties, kinetics, and vapor-liquid equilibrium are assumed so that the basic control issues of reactive distillation can be explored without being clouded by complexities of a specific chemical system. Six alternative control structures were evaluated via rigorous dynamic simulation. All of the schemes use a composition analyzer in the reactive zone to maintain stoichiometric balance was advocated. The interaction between design and control is illustrated by the impact of holdup in the reactive zone: increasing holdup (catalyst) improves the dynamic controllability of the process. A wide variety of quite large disturbances can be handled.

Al-Arfaj & Luyben (2002a) studied the control structures for ethyl *tert*-butyl ether (ETBE) reactive distillation columns. Two process configurations are explored: a design with two fresh reactant feed streams and a design with a single mixed reactant feed. A double-feed design is optimized and used in the control study, and single-feed design is used from the literature with some modifications. In the double-feed design, an excess of ethanol is not used, so the manipulation of one of the fresh feed streams is required to perfectly balance the stoichiometry of the reaction. Three basic control structures are studied. The first one used direct composition control of two product purities. The second structure fixes the reflux ratio and controls one end product. The third structure used temperature to infer product composition with a fixed reflux ratio. Temperature control provides fairly effective control provided disturbances are not too large.

Al-Arfaj & Luyben (2002b) studied the design and control of a methyl acetate reactive distillation column. Several steady-state multiplicities were found. The impact of these multiplicities on the openloop stabilities was discussed. The systems that are openloop unstable were more difficult to control than openloop stable systems. A control structure with one internal composition controller and one temperature controller provides the effective control of both systems for both high and moderate conversion designs. A two-temperature control structure is effective when the system is overdesigned in terms of number of reactive trays, holdup and/or catalyst load. Direct control of product purity for the high-conversion/high-purity design is difficult because of system nonlinearity and interaction. Tray temperature control avoids the nonlinearity problem.

Wang et al., (2003) analyzed an *n*-butyl acetate reactive distillation column under steady state condition and designed the control strategy of the column. Product quality is maintained by controlling the temperature of the stage inside the column that does not exhibit multiplicity when the reboiler duty is varied. Reboiler duty is used as the manipulated variable in the temperature control loop. The feed flow rates of *n*-butanol and acetic acid are controlled at a desired ratio. The set point of the ratio control is used as the manipulated variable in an inner cascade loop to control the acetic acid composition inside the column. This inner composition cascade loop guards against feed flow sensor bias in the feed-ratio control. The value of this composition set point is manipulated by an outer cascade loop that controls the composition of the bottom product. This outer cascade loop accounts for changes in reaction residence time relative to reaction time due to production rate changes or catalyst deactivation. The proposed scheme was able to reject various disturbances and maintain the desired high-purity and high-conversion operation.

Zeng et al., (2006) studied on the design and control of a reactive distillation column system for the production of butyl acrylate. The proposed design is quite simple including only one reactive distillation column and an overhand decanter. High purity butyl acrylate product (99.83 mol %) can be obtained from the bottom of the reactive distillation column. The other outlet stream of the system is the aqueous (95.9 mol $\%H_2O$) draw from the decanter. The optimal design and operating conditions

were obtained by minimizing the TAC value of the system. Output multiplicity of this system was also illustrated with reboiler duty or feed ratio as the bifurcation parameter. The stable steady state condition with the highest purity was selected as the reference for the control study. The proposed control strategy of this system contains only one tray temperature control loop to control sixth stage tray temperature by varying acrylic acid to butanol feed ratio while keeping the ratio of reboiler duty to the butanol feed flow at a constant value. No on-line composition measurement is needed in the overall strategy. The closed-loop dynamic simulations of the proposed control strategy under various disturbances including throughput change, feed composition variations, and catalyst decay disturbance were illustrated.

Hung et al. (2006b) explored the dynamics and control for the recovery of dilute acetic acid (ranging from 100 wt% to 30 wt %) via esterification using reactive distillation. The total annual cost (TAC) analysis shows that a standalone reactive distillation is more economical than a flowsheet with a pre-treatment unit. First, two measures are used to analyze the degree of nonlinearity for all four cases. Results show that significant nonlinearity and possible steady-state sign reversal are observed for all four systems. A systematic design procedure is used to design the control structures. Simulation results reveal that a dual-temperature control structure works reasonably well for all four cases, especially for 75 wt % and 50 wt % acetic acid feed. A feedfoward scheme is incorporated to improve the control performance and the results clearly show much improved control can be obtained for 100 wt % and 30 wt % acetic acid feed compositions. Finally, the one-temperature-one-composition control scheme is proposed and the offset-free composition responses are observed, however, with slower dynamics.