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## Recovery of Lactic Acid by Reactive Distillation

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**Abstract:** In many industrial processes, the intelligent integration of chemical reactions and separation in one unit (reactive distillation) process was found to be superior to conventional reactor-separator sequences with respect to their economic properties and environmental compatibility. On the other hand, lactic acid is potentially an important raw material for biodegradable polymers and its recovery from aqueous solution is highly difficult. The lactic acid can be recovered by using reactive distillation. In this study, the lactic acid recovery was carried out by reactive distillation using n-butanol as reactive entrainer. The effect of initial concentration, mole ratio and catalyst weight on removal of water from aqueous lactic acid solution were studied and optimum values evaluated.

**Key words:** Reactive distillation, lactic acid, n-butanol, amberlite catalyst, free lactic acid, poly lactic acid, total lactic acid, mole ratio, catalyst weight

### INTRODUCTION

Usually in the chemical industry, the conversion of substances and the separation of the desired products are carried out in sequential unit operations, especially if more than one main reactions and non-condensable gas are involved. In many cases the intelligent integration of chemical reactions and separation in one reactive distillation process was found to be superior to the conventional reactor-separator sequences with respect to their economic properties and environmental compatibility (Sundmacher and Kienle, 2003). Reactive distillation is a technique for combining a number of process operations in a single device. One company has developed a reactive distillation process for the manufacture of methyl acetate which reduces the number of distillation columns from eight to three, also eliminating an extraction column and a separate reactor (Agregda *et al.*, 1990; Doherty and Buzad, 1992; Siirola, 1995).

Inventory is reduced and auxiliary equipment such as reboilers, condensers, pumps and heat exchangers are eliminated. Figure 1 shows the conventional design and Fig. 2 shows the reactive distillation design. In most works of recent years reactive distillation technology was applied to increase the conversion of single equilibrium limited reactions with simultaneous separation of main and by-products.

Lactic acid is potentially an important raw material for biodegradable polymers such as polylactide. The conventional methods for the recovery of lactic acids are

precipitation, extraction with a solvent, electrodialysis and adsorption. However these recovery processes are not economical because of high cost and low purity of the recovered lactic acid. Lactic acid in high purity from aqueous solutions can be recovered by reactive distillation process. This process gives a good yield of lactic acid by carrying out esterification reaction, distillation and hydrolysis reaction simultaneously. The concept of reactive distillation for recovery of lactic acid by carrying out reaction and distillation is not new. This technique was first applied by Schopmeyer and Arnold (1944) for the continuous process. In this process the crude lactic acid reacts with low boiling aliphatic alcohol (methanol) in the presence of a homogeneous catalyst (sulfuric acid). Due to the corrosion and separation problems along with the occurrence of side reactions posed by the use of homogeneous catalyst this process it is difficult to use it on industrial level. Choi and Hong (1999) have developed batch reactive distillation system using cation exchange resins to overcome the above problem. The system consists of esterification and hydrolysis reactor along with a fractionating column as shown in Fig. 3.

Esterification of crude lactic acid with methanol is takes place in the esterification reactor. The vapors containing unreacted methanol, water and product methyl lactate pass through the fractionating column. Methyl lactate and water being low volatiles get condensed in the partial condenser and flow downward towards the hydrolysis reactor. Hydrolysis of methyl lactate gives

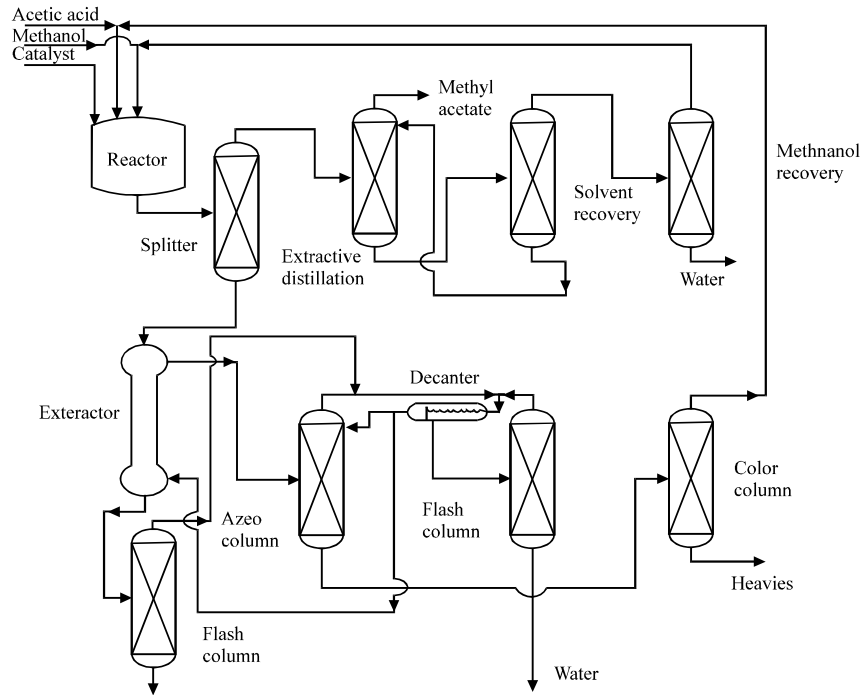


Fig. 1: Conventional design for manufacture of methyl acetate (Based on Siirola, 1995)

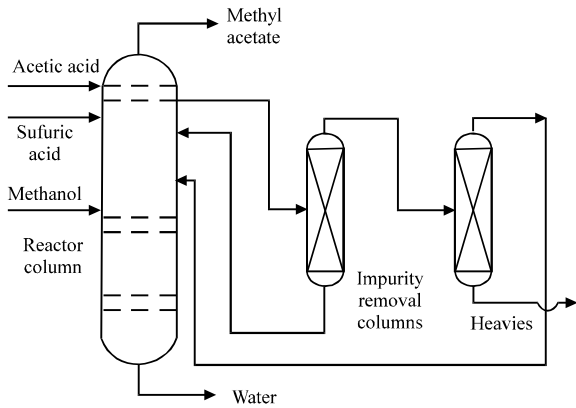


Fig. 2: Reactive distillation process for manufacture of methyl acetate (Agreda *et al.*, 1990)

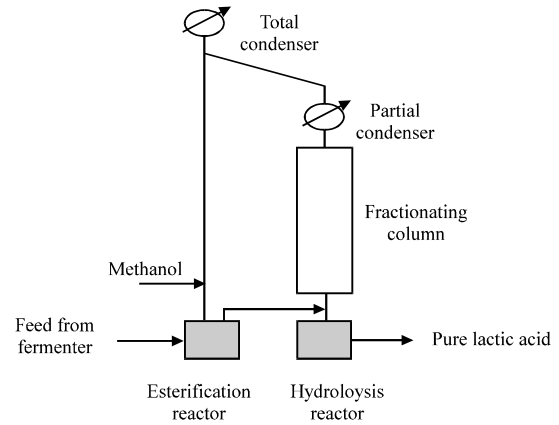


Fig. 3: A conceptual block flow diagram for lactic acid recovery from the fermentation product (Choi and Hong, 1999)

methanol and lactic acid. Lactic acid being non-volatile remains in the reactor, but methanol vapors move upward and get condensed in the total condenser. This methanol is recycled back to the esterification reactor. Yield of lactic acid thus obtained is 95%. This is a novel concept and can be effectively used for recovery of many high boiling compounds obtained in biochemical or chemical reaction.

Esterification of lactic acid with n-butanol may be performed to synthesize n-butyl lactate or to recover lactic acid from its aqueous solution. The percentage recovery

of Lactic acid highly depends on type of alcohol used in the operation. Butanol is found to be more useful since it doesn't allow polymerizing the Lactic Acid. Therefore, the effective method of recovery of lactic acid is that the lactic acid is reacted with butanol and butyl lactate is produced by the esterification reaction. Then butyl lactate is distilled with the hydrolysis reaction into lactic acid. In the present work, some studies on the effect of mole ratio, catalyst loading on the conversion of lactic acid to butyl

lactate by esterification have been conducted. Further, the effects of operating parameters like feed mole ratio and catalyst loading are evaluated on the conversion of lactic acid in batch reactive distillation. Optimum operating conditions are obtained from experimental results. A continuous reactive distillation process for the recovery of lactic acid is proposed.

## MATERIALS AND METHODS

**Materials:** The esterification reaction of lactic acid and butanol is conducted in the presence of Amberlite (MERCK) catalyst in a batch reactive distillation apparatus with Glass Packed column (Borosil). The lactic acid and butanol used in the experimental work are obtained from MERCK. The experimental set-up used is shown in Fig. 4. The experimental setup consists of 500 mL three necks round bottom flask placed on a heating mantle with magnetic stirrer. The openings of three neck flask are used for thermo well for placing thermometer, second opening was connected to column (diameter of column = 3 cm, length of column = 30 cm), packed with glass rasching rings (diameter = 2 mm and length = 3 mm) and other for fixing silicon rubber with syringe for collecting sample. A double surface condenser was arranged on the column for condensing the vapors for recycle. The condensed vapors are allowed settled in a glass tube attached to the column. The water and butanol separate there according to density difference. Water is

removed from the lower layer and butanol is sent back into column. The entire packed column from flask to condenser is thermally insulated to avoid heat losses. The condenser cooling water is circulating by means of a pump.

Double surface condensers are used for efficient condensing the vapours in the operation. The entire setup including packed column is properly insulated to avoid heat losses. The batch reactive distillation is done under total reflux conditions. However, the set up facilitates to collect the water from condensate and separates continuously.

**Methods:** Lactic acid with required quantity of butanol for the desired mole ratio along with quantity of catalyst percentage are charged to the three neck flask, after mixing the contents are heated to generate vapors to pass through the packed column for the separation of water by condensing from the more volatile products. The residue samples were taken for different times to analyze the Free Lactic Acid and Total Lactic Acid mole fractions. The condensed liquid from the condenser is allowed to pass through a separator to collect water at the bottom of a graduated tube with a drain tap and the top liquid is completely as reflecting to the column. The process was continued to collect the water up to a point where the removal of water is very slow.

### Analysis

**Total lactic acid (TLA):** Weighed amount of the sample is taken into a 100 mL conical flask and 25 mL of water is added. Now 30 mL of standard 0.5 N aqueous NaOH is added to the flask. The solution is placed on a heater and brought to slow boil for 2 min. The sample is allowed to cool and the excess NaOH is titrated with standard 0.5 N HCl to the first disappearance of pink color with phenolphthalein indicator.

$$\text{Total acidity as wt\%} = \frac{(V1N1 - V2N2) \times 90.08 \times 100}{(W \times 1000)}$$

**Free lactic acid (FLA):** Weighed amount of the reactor sample is taken into the conical flask and 25 mL of water is added. The solution is titrated with 0.5 N standard solution to the first appearance of pink color with phenolphthalein indicator.

$$\text{Total free acidity as LA WT\%} = \frac{(V1N1 \times 90.08 \times)}{(W \times 1000)}$$

## RESULTS AND DISCUSSION

**Effect of mole ratio:** The simple distillation of lactic acid solution to separate water from the system has two

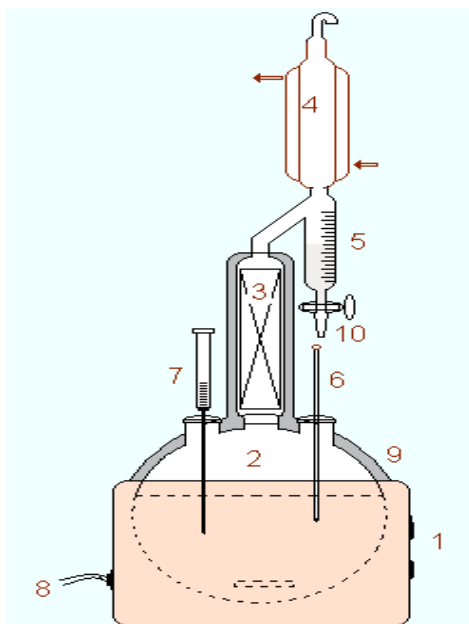


Fig. 4: Schematic diagram of experimental set-up

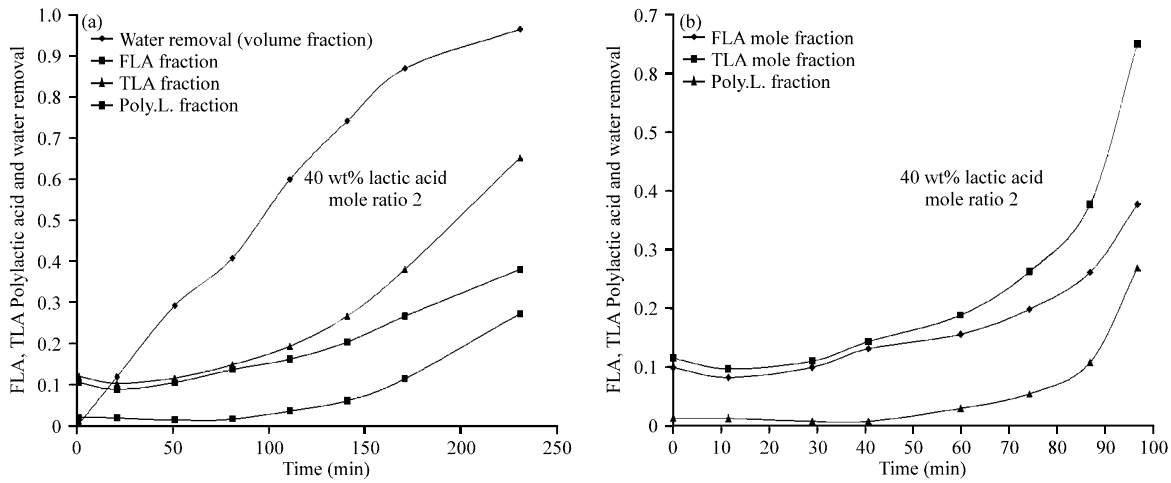


Fig. 5(a-b): Variations in concentrations of Free Lactic Acid (FLA), Poly Lactic Acid (PLA) and Water removal with Time

disadvantages. One is the amount of polylactic acid increases continuously as water is removed. Second one is the rate of removal of water vapors is slow comparatively when using butanol. After removing 53% of water the rate of removal of water is slow. The plots Fig. 5a, b are drawn for variation of poly lactic acid with time and water removal. As the time passes the temp of boiling mixture will also increases. The sudden changes occurs in the system depends on % water removal and the amount of butanol present in the system. The gap between Free Lactic Acid (FLA) and Total Lactic Acid (TLA) curves is nothing but poly lactic acid. As water is removed the lactic acid concentrates and come close together and polymerization starts.

However it is observed that reactive distillation of lactic acid, using n-butanol overcome the above disadvantages. In Fig. 5b for the mole ratio 2, it is observed that there is no change in poly lactic acid amount up to the removal of 60% of water. Then its value increases. This is mainly depends upon the amount n-butanol present in the system. In the water removal also it makes a considerable change. Therefore water can be removed up to 94% without polymerization reaction in the operation.

Experiments were done for different mole ratios of 1, 1.5, 2 2.5 and 3. In these experiments the removal of water was not influenced by mole ratio upto the removal of 40% (Fig. 6). The rate of removal of water increases with increasing mole ratio. The amount of poly lactic acid reduced to a lower value then it increases for each mole ratio. The increase is mainly due to the reduction of butanol present in the system. The minimum Poly lactic acid formed for mole ratio 2 with maximum amount of water removed. Therefore, the mole ratio 2 is optimum for the operation.

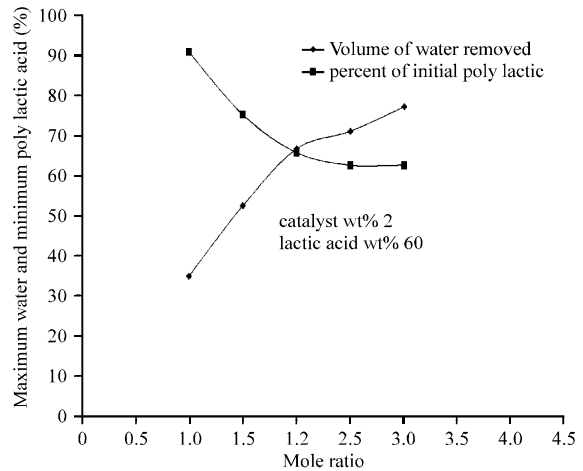


Fig. 6: Influence of mole ratio on formation of Poly Lactic acid

**Effect of catalyst weight:** Figure 7 shows the advantage of using Amberlite catalyst in reactive distillation. The figure shows clearly that the Amberlite catalyst reduces the amount of formation of Poly Lactic Acid to a lower value than for without catalyst. The catalyst is reducing 15% of poly lactic acid formation than without catalyst and therefore catalyst is useful in the operation.

Figure 8 shows the effect of catalyst weight percent. As catalyst weight percent increases the Poly Lactic Acid reduced to low value and water removed increases to maximum. The minimum Poly Lactic Acid is formed in the system for 2 weight percent to 3 weight percent but after 3 weight percent its formation remains constant. It may be due to the formation of equilibrium between Free Lactic Acid and Poly Lactic Acid. Therefore, the 3 weight percent catalyst is optimum in the operation.

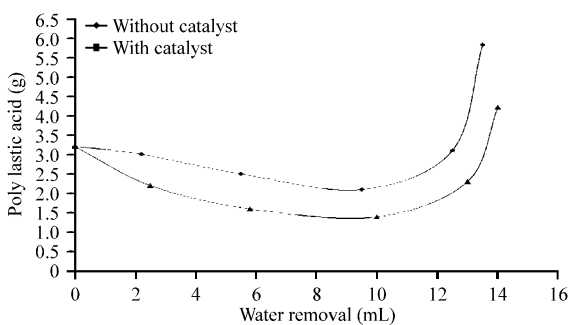


Fig. 7: Advantage of amberlite catalyst

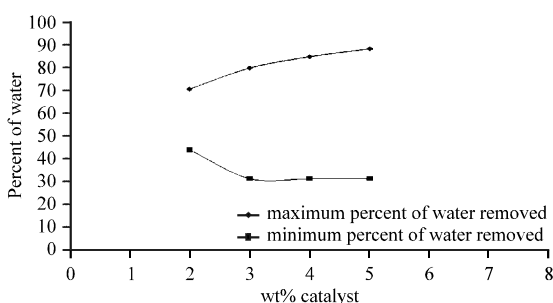


Fig. 8: Effect of catalyst weight on removal of water

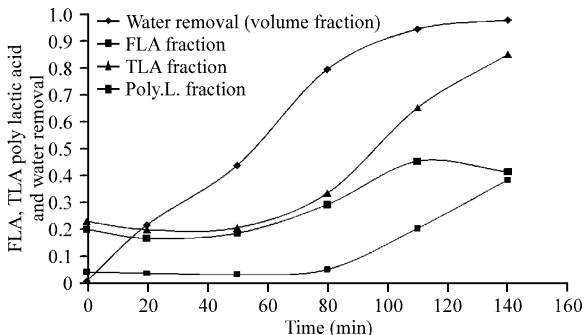


Fig. 9: Operation dynamics at optimum conditions

**Recovery of lactic acid at optimum conditions:** Using optimum conditions such as mole ratio 2 and catalyst weight percent 3 are used in the operation and water was removed. Figure 9 shows the water removal and poly lactic formation. One can see from Fig. 9 that it is easy to remove 80% water without formation of Poly Lactic Acid. Initially the Free Lactic Acid and Total Lactic Acid mole fractions decreased then increases. This means the rate of decrease of Free Lactic Acid is more than rate of removal of water. Then the Total Lactic Acid continuously increases where as Free Lactic Acid increases up to certain level and then decreases. Therefore, after removing 90% of water, the Free Lactic Acid is converted into Poly Lactic Acid. The gap between Free Lactic Acid

and Total Lactic Acid curves will give the Poly Lactic Acid. The increase in the Poly Lactic Acid mainly depends upon the amount of n-butanol present in the system.

## CONCLUSION

The importance of reactive distillation has been emphasized. Recovery of lactic acid from aqueous solution is experimentally carried by using batch reactive distillation. It is observed from the initial experimental data obtained that as the water removal increases with time, the percentage of free lactic acid and total lactic acid increase. Also, as the weight of the catalyst increased, the yield of recovered lactic acid is increased. In the esterification reaction it is observed that as the feed concentration of the lactic acid and the reactant molar ratio decrease, the recovery yield of the lactic acid increased. The yield of recovered lactic acid is estimated as high as 95% in the operation when all the evaporated water is condensed and removed from the system. For 60 weight percent lactic acid aqueous solution the optimum operating conditions are found to be 2 mole ratio and 3 weight percent of catalyst.

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## REFERENCES

- Agreda, V.H., L.R. Partin and W.H. Heise, 1990. High-purity methyl acetate via reactive distillation. *Chem. Eng. Prog.*, 86: 40-46.
- Choi, J.I. and W.N. Hong, 1999. Recovery of lactic acid by batch distillation with chemical reactions using ion exchange resin. *J. Chem. Eng. Jpn.*, 32: 184-189.
- Doherty, M.F. and G. Buzad, 1992. Reactive distillation by design. *Trans. Inst. Chem. Eng. A*, 70: 448-458.
- Schopmeyer, H.H. and C.R. Arnold, 1944. Lactic acid purification. U.S. Patent No. 2, 350, 370.
- Siirola, J.J., 1995. An industrial perspective on process synthesis. *AIChE Symp. Ser.*, 91: 222-233.
- Sundmacher, K. and A. Kienle, 2003. *Reactive Distillation: Status and Future Directions*. Wiley-VCH, Weinheim, Germany, ISBN-13: 978-3527305797, Pages: 308.