Study of Performance of Packed Bed Reactive Distillation Column for the Esterification Process

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ABSTRACT
In this effort, the batch reactive distillation performance was studied by the production of butyl acetate in a batch packed bed reactive distillation column. Esterification of butan-1-ol with acetic acid to produce butyl acetate and water with homogenous hydrochloric acid as a catalyst was considered. This system was chosen because the reaction is reversible and the boiling point of reactants and products are different. The reaction was carried out with and without a distillation column and shows that the reactive distillation is more efficient from the conventional process (reactor and then separation). The concentration of butyl acetate increases from 12.38% to 31.74% at the best condition of feed mole ratio of 2.

KEYWORDS: *Acetic acid, butan-1-ol, esterification, butyl acetate, catalyst, reactive distillation*

INTRODUCTION

Distillation is one of the most important separation processes in chemical and process industry. All around the globe, almost all the chemical industries have a significant fraction of capital investment and operating cost involves in distillation separation processes. As a result, any form of improvement of distillation operation can be very beneficial economically. Reactive distillation (RD) is one major step in achieving these goals. In recent years, RD has gained increased attention because of its high potential for process intensification. It is applicable to certain reactions where the maximum conversion is limited by chemical equilibrium in conventional reactors. General application of reactive distillation is the separation of a close-boiling or azeotrope mixtures. A second application of reactive distillation involves taking into account undesirable reactions that may occur during distillation, but the most interesting application involves combining chemical reactions and separation by distillation in a single distillation apparatus. It offers various advantages compared to the conventional processes of the reactor followed by separation in different units. This reduces or eliminates reactor, recycle costs and ensures lower utilization of energy resources.

These processes as a whole are not a new concept as the first patent dates back to the 1920s. The idea of Reactive Distillation was proposed in 1921 by Backhaus and verified by Leyes and Othmer by performing an esterification reaction of acetic acid with an excess of n-butanol at acidic conditions to produce butyl acetate. They achieved desirable chemical reactions and separation by distillation in a single distillation process. While the concept existed much earlier, the first real-world implementation of reactive distillation took place in the 1980s (Zoeller, n.d.). One of the well-known Reactive Distillation processes is the Eastman Chemical Company's methyl acetate process. By making methyl acetate through Reactive Distillation instead of the conventional process, seven major units are replaced by one single unit. The old technology of that company was complicated and expensive due to the presence of multiple azeotropes. (J. D. Seader,Ernest J. Henley and D. Keith Roper, n.d.). To get pure products from a mixture, azeotropes have to be broken. In the Reactive Distillation process, the azeotrope is broken because one of the reactants works as an extractant and the products are separated immediately.

During the reactive distillation process,

the chemical reaction usually takes place in the liquid phase in the tray columns or at the surface of a solid catalyst in a packed bed column with a liquid phase. Reactions limited by chemical equilibrium constraints will be forwarded if the products can be continuously removed from the reactor environment, thus shifting the direction of the equilibrium reaction towards the products side.

MATERIAL AND METHODS

Materials and catalyst

A batch reactive distillation column was set up for this work using glassware available in the chemistry laboratory. Batch RD column has 3 sections. These include two-neck round bottom flask (with a capacity of 500 ml) serving as both reactor and reboiler, rectifying section serving as a separation unit and condenser used to cool the top product.

The rectifying section was packed with glass rings. Each ring had a 6mm diameter and an average length of 6 mm. Mole ratio of acetic acid to butanol-1-ol, catalyst (HCl) loading and heating element duty were systematically varied to maintain the temperature to study the acetic acid conversion and butyl acetate purity in the bottom product.

Procedure

Performance of the RDC was planned to study by measuring the volume of butyl acetate produced from

1. With and without reactive distillation technique of esterification with the homogeneous catalyst HCl.
2. Effect of Feed molar ratio of butan-1-ol to acetic acid as 1, 1.5, 2, 2.5 and 3 with and without homogeneous catalyst HCl.

To start the experiment, the flask (reboiler) was filled with a specific molar ratio of acetic acid and butan-1-ol. Then the heater was switched on. As the reboiler started heating, the vapors from the reaction mixture in the reboiler started to rise through the packing where heat and mass transfer occurs. Finally, the reaction mixture reached the condenser, where the condensed vapor (distillate) started was collected. Operating temperature was maintained at a constant level by switching the heating mantle on and off. The column operated for 20 min under total reflux. After 20 minutes, the first sample was collected from the reboiler section as the bottom product. Then all samples were collected with a 10-minute interval until a total time of 60 minutes. The samples were analyzed for their composition. This was done by titration initially.

Chemical analysis

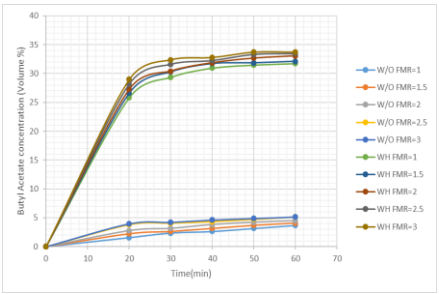
Chemical analysis is used to determine the compositions of samples collected. Before starting the experiment, standard solutions of hydrochloric acid (1M) and sodium chloride (1M) were prepared. Acetic acid and butyl acetate compositions can be determined using standard solutions. To determine the amount of acetic acid, the sample can be titrated with the standard solution of sodium hydroxide using phenolphthalein solution as the indicator. The result of the titration can be calculated to find the acid value.

To determine the butyl acetate amount, excess standard solution of sodium hydroxide is mixed to a neutralized solution of sample. The mixture is heated under reflux for 30 minutes to allow the saponification reaction. At the end the excess of alkali can be titrated immediately with standard solution of hydrochloric acid using phenolphthalein solution as the indicator. The result of the titration can be utilized to determine the excess base that was not consumed, which is then used to determine the ethyl acetate amount consumed during the saponification reaction. (D.O. Araromi,

2Sonibare J. A, Emuoyibofarhe O Justice, and T.J. Afolabi, 2011)

RESULTS AND DISCUSSION

We can clearly indicate that, with the presence of the catalyst HCl, concentration of butyl acetate increased during the reactive distillation procedure compared to the conventional esterification procedure. (See Figure 1)



SUMMARY

From this work, the following conclusions are made:

1. The reactive distillation is more efficient than the conventional process. Reactive distillation procedure results in the highest production of butyl acetate than that of the conventional process (12.38% to 31.74%).
2. The concentration of butyl acetate increases with the increase of feed mole ratio.
3. The concentration of butyl acetate increases with time and then reaches an almost constant concentration.
4. The optimum butyl acetate in the product was obtained at feed mole ratio 2.

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Figure 1