Simulation of Butyl Acetate and Methanol Production by Transesterification Reaction via Conventional Distillation Process

Nikhil V. Sancheti
Department of Chemical Engineering
L.I.T., Nagpur, Maharashtra, India

Sanjay P. Shirsat
Department of Chemical Engineering
L.I.T., Nagpur, Maharashtra, India

Dnyaneshwar D. Awachar
Department of Chemical Engineering
L.I.T., Nagpur, Maharashtra, India

Abstract- A Simulation based design method is studied for production of n-butyl acetate and methanol by transesterification reaction of methyl acetate and n-butanol by conventional distillation process. The reaction is catalyzed by sulphonic ion resin (Amberlyst 15) forms two azeotrope, for separation of such complex azeotropic mixture by a conventional process series of distillation columns are required. A conventional process for production of butyl acetate includes a reactor and three distillation columns. The equilibrium based data for liquid phase sulphonic ion resin as catalyst and modified uniquac is implemented to ascertain the steady state performance of conventional process .To produce high purity products at end of the distillation columns a model with an equilibrium reactor and three distillation columns is simulated using ChemCad software. Effect of various parameters such as reflux ratio, number of stages, reboiler duty is studied to find out optimum operating condition.

Keywords – Transesterification, Conventional, ChemCad, reflux ratio

I. INTRODUCTION

The n-butyl acetate, which is achromatic and transparent liquid, primarily it is used in paint and coating manufacture and the lacquer industry. *n*-butyl acetate is not only used as intermediate in organic synthesis and in the photographic industry but also used as an extracting agent. Furthermore n-Butyl acetate is used as solvent (for acrylic polymers, vinyl resins, and leather dressings in cosmetic formulations) and dehydrant in chemical industry. It is also used as a reaction medium for adhesives. Methyl acetate is a byproduct in the industrial manufacturing process of poly vinyl alcohol (PVA). For one ton of PVA, 1.68 tons of methyl acetate is produced. Methanol is a feed stock of PVA production, because the industrial application of methyl acetate is limited, the transesterification of methyl acetate with n-butanol forming n-butyl acetate and methanol was chosen due to economic interests, a low reaction rate and an equilibrium constant close to unity lead to a large number of stages in a distillation process.

Because of its lower impact on the environment, *n*-butyl acetate is able to replace the toxic and teratogenic ethoxy ethyl acetate that is often used as a solvent [1]. Investigations of different process alternatives for the production of *n*-butyl acetate have been performed by Hartig and Regner [2] and Block and Hegner [3].These authors considered the homogeneously catalyzed reaction. Jimenez and Costa-Lopez presented two papers on the production of butyl acetate and methanol by reacting methyl acetate and butanol in a reactive distillation column [4-5]. In their first paper, Jimenez and Costa-Lopez gives useful information dealing with reaction kinetics. In their second paper, they study a four-column process in which the key unit is a reactive distillation column. The presence of a minimum-boiling azeotrope between methyl acetate and methanol prevents the use of just a single reactive column because any unreacted methyl acetate that leaves the reaction zone will go out the top of the column with the methanol. Also Jimenez and Costa-Lopez1 claim that an extractive agent (*o*-xylene) must be added to the reactive distillation column. Of course, this means that the entrainer must recover in a subsequent column. Luyben et.al. [6], has stated a conventional process with a reactor and three distillation columns, in which reactants leaving the reactor

are recovered and recycled and methanol and butyl acetate products are produced at 99% purity, further they showed that use of entrainer is not necessary. Ewa Bozek-Winkler and Jurgen Gmehling proposed equilibrium data for the temperature range 104°F to 135°F. Ewa Bozek-Winkler and Jurgen Gmehling proved that with increase in temperature, the reaction rate increases, but nearly the same equilibrium conversion of methyl acetate is obtained [7].

This paper presents a systematic approach for transesterification reaction catalyzed by sulphonic ion resin (Amberlyst 15) for the production of *n*-butyl acetate using reliable thermodynamic, kinetic data and equilibrium data. Authors have used equilibrium data for conversion of methyl acetate to butyl acetate. Finally, simulation studies can be used to identify the roles of important design parameters (e.g., numbers of stages, location of feed positions, reflux ratio) and to propose an optimal setup.

II. CHEMICAL EQUILIBRIUM AND KINETICS

A. The liquid-phase reversible reaction considered is

Methyl acetate + n-butanol ↔ n-Butyl acetate + methanol

n-butanol and methyl acetate are the high and low boiling reactants, *n*-Butyl acetate and methanol are the high and low boiling products, respectively. The yield for the transesterification reaction is strongly limited by the equilibrium conversion. This reversible reaction needs to be catalyzed by strong acids. Kinetic data for a sulfonic ion-exchange resin, Amberlyst 15, were reported by Jime´nez, Garvin, and Costa-Lo´pez (2002) [4] Ewa Bozek-Winkler and Jurgen Gmehling carried an experiment to predict the equilibrium data for the temperature range 104°F to 135°F. The temperature dependence of the equilibrium constant can be expressed by $\ln K_a = 0.8158 - 267.9/T$, since it has been proved that reaction rate increases with increase in temperature, but nearly same conversion occurs with increased temperature. The temperature in the reactor of the conventional process is set at 200 °F, and this is also about the temperature that occurs in the reactive zone of the reactive distillation column when operating at 15 psia in the condenser [7].

The main drawbacks of ion-exchange resin catalyst were the low thermal stability, need for catalyst containers to improve mechanical properties, and possible diffusion problems resins are also susceptible to both short-term poisoning and long-term deactivation. One of the possibilities to obtain the desired products would be the transesterification of methyl acetate with *n*-butanol, which leads to *n*-butyl acetate and methanol. Separation becomes more complex because of two binary maximum pressure azeotropes, namely, methanol-methyl acetate and n-butanol-n-butyl acetate. Additionally, the low chemical equilibrium constant (close to unity) would result in low conversion and high capital costs.

B. Vapour-Liquid Equilibrium-

Because of the existence of two binary azeotropes, the phase equilibrium of this four-component system is complex. Using NRTL physical properties (as recommended by Jimenez and Costa-Lopez1), Aspen Plus predicts two binary azeotropes: (1) Methyl acetate and methanol form a homogeneous minimum-boiling azeotrope with a composition of 66 mol % methyl acetate and 34 mol % of methanol at 15 psia and 129.5°F. (2) Butanol and butyl acetate form a homogeneous minimum-boiling azeotrope with a composition of 78 mol% butanol and 22 mol % of butyl acetate at 15 psia and 242.4°F. As the pressure is raised to about 50 psia, the azeotrope disappears. The first azeotrope means that any columns that are separating methyl acetate from methanol can only produce a distillate, which has a composition near to the azeotropic composition and can produce high-purity methanol in the bottoms, in this work, these columns are specified to produce a distillate with a composition of 65 mol % methyl acetate. Note that a column pressure of 15 psia permits the use of cooling water in the condenser. The second azeotrope has unusual pressure dependence. In most chemical systems, increasing pressure moves the composition of the azeotrope to the left (becomes less rich in the lighter component). However, the opposite effect is displayed in the butanol/butyl acetate system, in this study, the columns separating butanol and butyl acetate are operated at 15 psia, and this would reduce the per-pass conversion and require larger recycle flows.

III. Simulation and Result

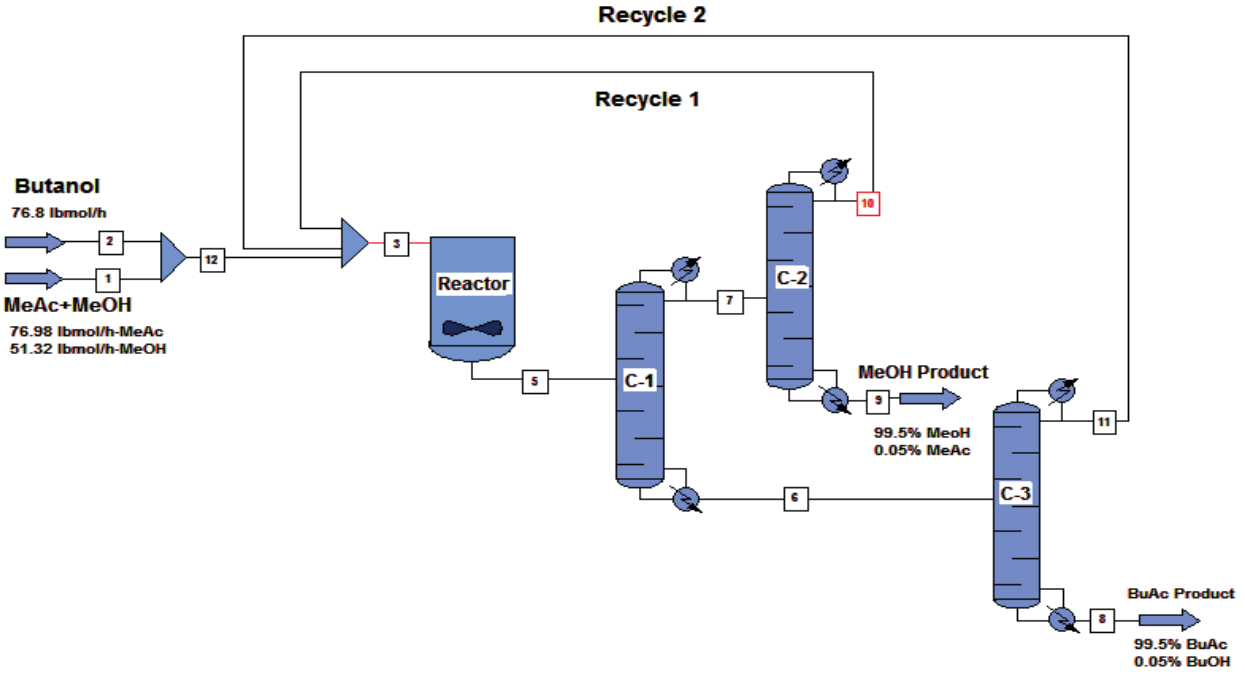


Figure 1.Flowsheet for Butyl acetate production

In the study, some design parameters about column geometry are determined by the criterion that the flood percent on each stage, calculated by using the sizing function provided by ChemCad software, is guaranteed not to exceed 75% at the nominal operating conditions. Thermodynamic aspect of Modified UNIQUAC is used for simulation purpose. The first two columns are sized with diameter 8.5 feet and a third column with diameter 6 feet. Each column is assumed to be tray columns. Figure 1 gives a sketch of the optimum conventional process studied in this paper. Flowsheet stream conditions, equipment sizes, and reboiler heat duties are provided. Fresh feed with a composition of 60 mol % methyl acetate and 40 mol % methanol and a flow rate of 128 lbmol/h is fed into a 200-ft3 equilibrium reactor, which operates at 200 °F and 100 psia. Fresh butanol (76.8 lbmol/h) is also fed to the equilibrium reactor, along with a butanol recycle stream (244.3 lbmol/h, 72.5 mol % butanol, 27.4mol % butyl acetate) and a methyl acetate/methanol recycle (130 lbmol/h, 67.16 mol % methyl acetate, and 32.84 mol % methanol). The per-pass conversion of methyl acetate is about 42%. An amount of heat (6.87×10^6 Btu/h) must be added to the reactor. Reactor effluent is fed to column C-1 in which methyl acetate and methanol are taken overhead and butanol and butyl acetate leave in the bottoms. The column has 28 trays including reboiler and condenser. The specifications for this column are 0.01 mol % methanol in the bottoms. The required reflux ratio is 1.5, and the reboiler heat duty is 16.39×10^6 Btu/h. The column operates with a condenser pressure of 15 psia, which gives a reflux drum temperature of 130 °F and permits the use of cooling water in the condenser. The distillate stream is fed to column C2, which produces high-purity (99.5 mol %) methanol in the bottoms and a distillate stream whose composition (67.2 mol % methyl acetate) is near that of the azeotrope. The distillate is recycled back to the reactor at a rate of 130 lbmol/h. The column has 27 trays including condenser and reboiler. To achieve these specifications, the reflux ratio is 1.7, and the reboiler heat duty is 32.58×10^6 Btu/h. The column operates with a condenser pressure of 15 psia, which gives a reflux drum temperature of 130 °F and permits the use of cooling water in the condenser. The bottoms from C1 is fed to column C3, which produces high-purity (99.5 mol %) butyl acetate in the bottoms and a butanol-rich 72.5 mol %) distillate that is recycled back to the reactor at a rate of 244.3 lbmol/h. The column has 63 trays condenser and reboiler. To achieve these specifications, the reflux ratio is 2.8, and the reboiler heat duty is 9.88×10^6 Btu/h. The column operates with a condenser pressure of 15 psia. The total energy consumption of the three columns in this conventional process is 58.85×10^6 Btu/h.

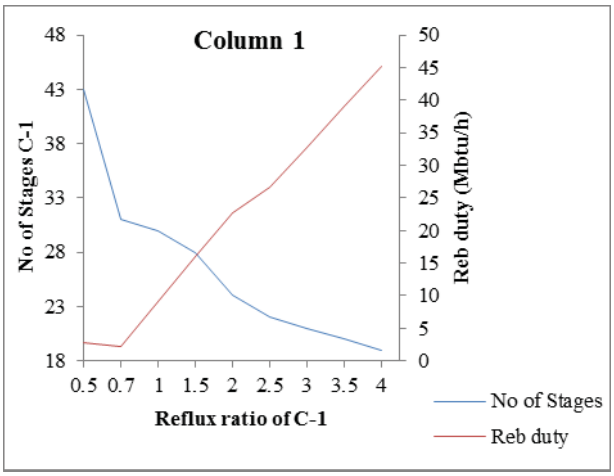


Figure 2.Optimum Reflux Ratio for Column 1

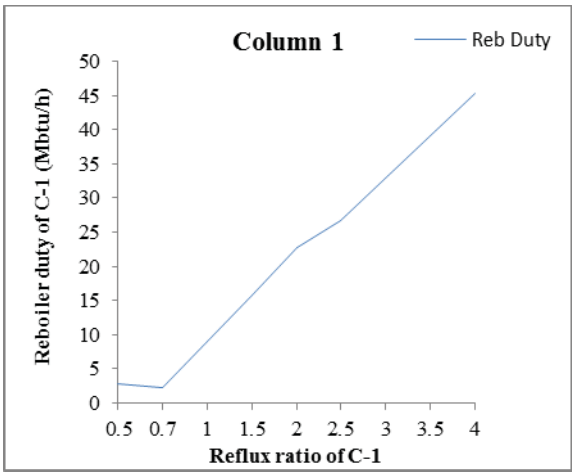


Figure 3.Effect of Reflux on Reboiler duty

Figure 2, 5, 8 shows graph plotted as reflux ratio on x-axis and no of stages and reboiler duty for each column on y-axis. The optimum condition is obtained from intersection of curves for reboiler duty and no of stages respectively, the optimum reflux ratios for each column are taken from graphs (figure 2, 5, 8). And effect of reflux ratio on reboiler duty and no of stages are plotted on graph (figures 3, 4, 6, 7, 9, 10). Optimum parameters for given process are found as, reflux ratio-1.5, 1.7, 2.8, no of stages-28, 27, 63 of column 1, 2, 3 respectively. And reboiler duty required for column 1, 2, 3 is 16.32, 32.58, 9.88 MBtu/h respectively.

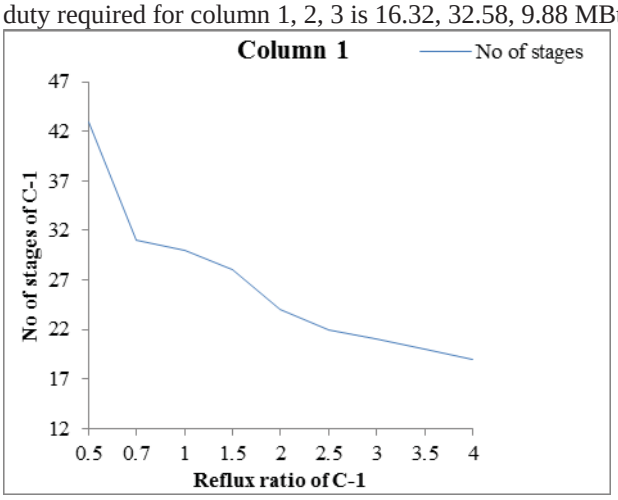


Figure 4.Effect of Reflux on no of stages

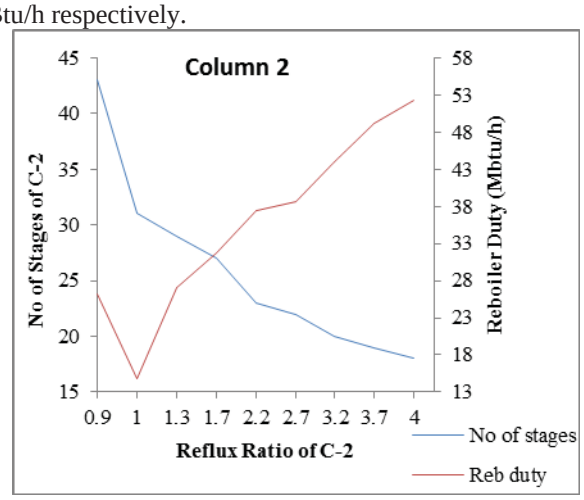
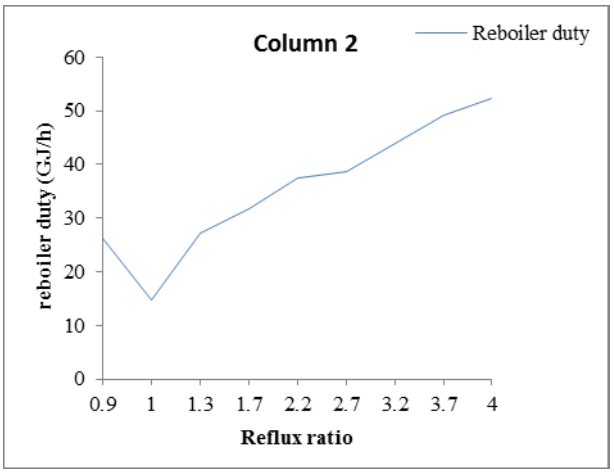


Figure 5.optimum Reflux Ratio for Column 2



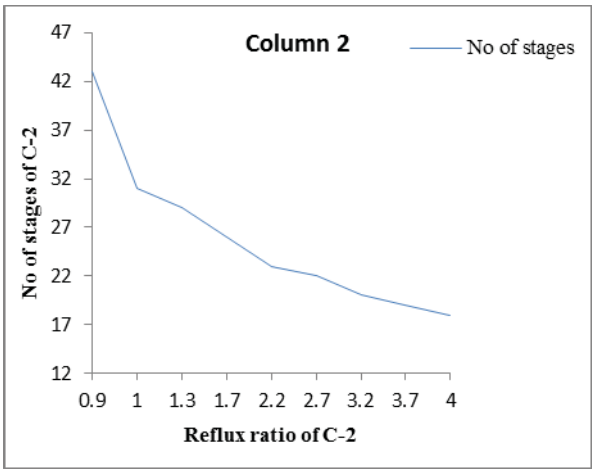


Figure 6.Effect of Reflux on Reboiler duty

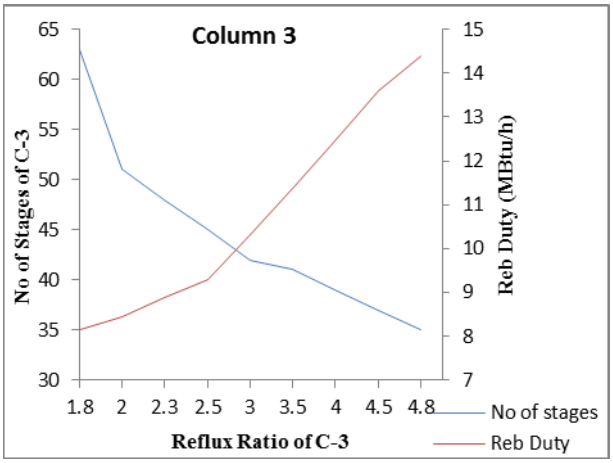


Figure 8.Optimum Reflux Ratio for Column 3

Figure 7.Effect of Reflux Ratio on no of stages

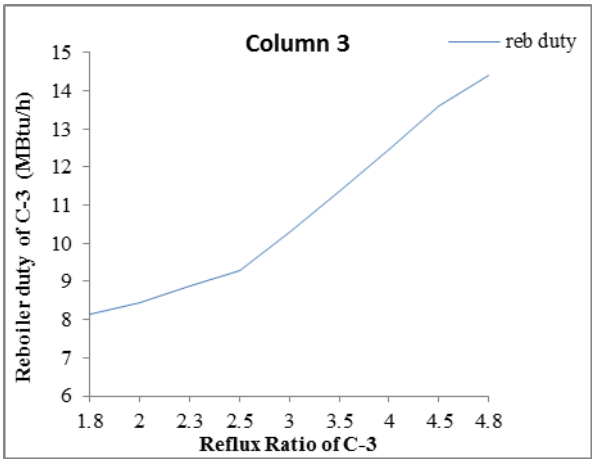


Figure 9.Effect of Reflux on Reboiler duty

Figure 11 shows the temperature profile of each column, which was directly obtained using plot function in Chemcad Software, from which it is clear that the column 3 can be used for heat integration purpose. Figure 12 and 13 gives the composition profile of products (n-butyl acetate, methanol) and reactants (methyl acetate, n-butanol) respectively. Methanol concentration in column 1 increases from stage 14 to stage 12 then gradually decreases up to azeotropic concentration at top of column. Methanol concentration increases up to stage 23, as output of reactor enters the column at 14 stage. After that methanol concentration nearly goes to zero in stripping section. A methanol and n-butyl acetate concentration in columns 2 and 3 respectively goes on increasing.

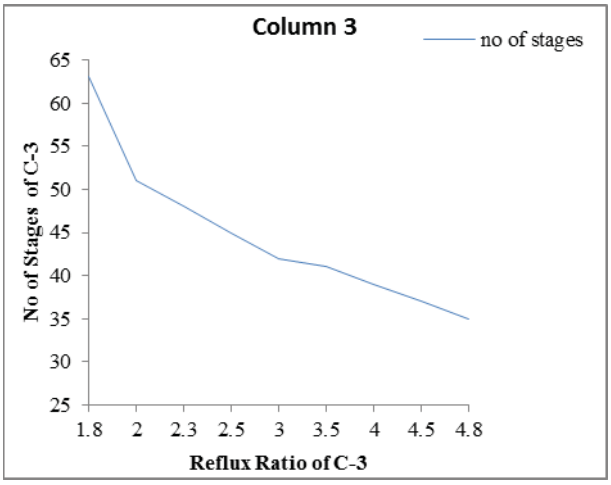


Figure 10.Effect of Reflux Ratio on no of stages

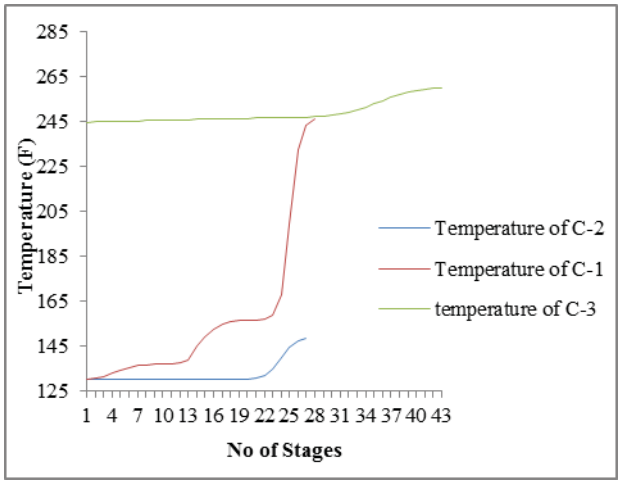


Figure 11.Temperature Profile

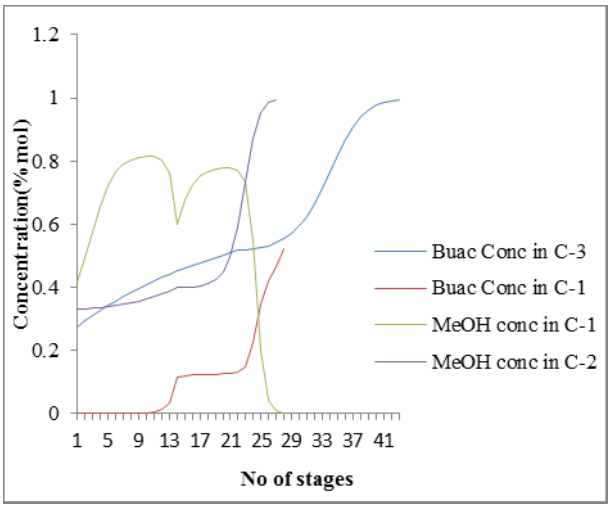


Figure 12.composition profile of Product

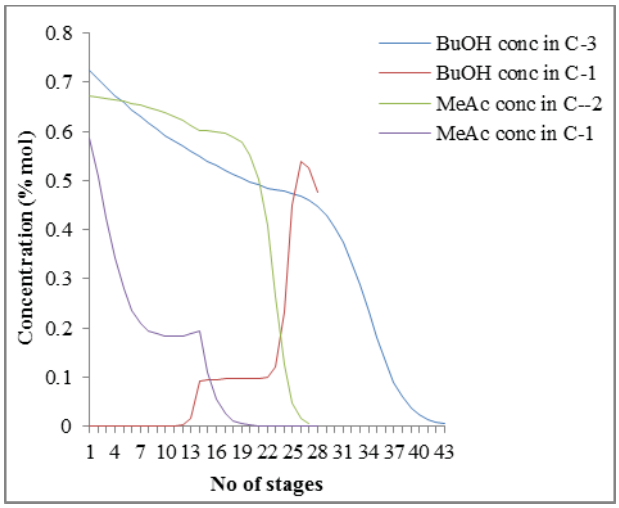


Figure 13.composition profile of reactant

IV.CONCLUSION

In the simulation study for production of n-butyl acetate and methanol by transesterification reaction of methyl acetate and n-butanol using Amberlyst 15 as a catalyst, by conventional process high purity products are obtained. A simulation was carried out using equilibrium data and thermodynamic model of Modified UNIQUAC. Optimum value for various parameters such as reflux ratio, number of stages and reboiler duty required for this separation were determined in this paper. Effect of reflux ratio on number of stages and reboiler duty were also presented.

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