

# Simulation of Transesterification Reactive Distillation with Total Thermal Coupling

Dnyaneshwar D. Awachar

*Department of Chemical Engineering  
L.I.T., Nagpur, Maharashtra, India*

Sanjay P. Shirsat

*Department of Chemical Engineering  
L.I.T., Nagpur, Maharashtra, India*

Nikhil V. Sancheti

*Department of Chemical Engineering  
L.I.T., Nagpur, Maharashtra, India*

**Abstract - In the study, simulation of a reactive distillation process with thermal coupling for the production of methanol and n-butyl acetate by transesterification reaction of methyl acetate and n-butanol are investigated. Since methanol and methyl acetate formed an azeotrope, the products of a reactive distillation column include n-butyl acetate and the mixture of methanol and methyl acetate, which must be separated by an additional column. Thermal coupling can be used to eliminate the condenser and reboiler required of the first column. When we compare this with conventional process we came to conclusion that this process requires not only energy reduction but also better operability can be obtained for the thermally coupled reactive distillation process.**

**Keywords: Reactive distillation, divided wall column, Chemcad.**

## I. INTRODUCTION

One important target of development of new processes is the reduction of energy and a reduced number of equipment compared to established processes. Developing such improved processes by process integration can successfully be carried out by combining unit operations in one apparatus. Well known integrated processes are Reactive Distillation (RD) that can be beneficial for both reaction and separation and the Divided Wall Column (DWC) which is used to carry out several distillation steps in one column. The combination of both Reactive Distillation and Divided Wall Column in one apparatus leads to the Reactive Divided Wall Column (RDWC). Kaibel (1987)[1] patented the dividing wall distillation column shown in Fig. 1, which is thermodynamically equivalent to the Petlyuk distillation column studied by Petlyuk et al. (1965)[2]. However, this equivalence is only valid when there is no heat transfer across the dividing wall.

One of the processes that can make effective use of reactive distillation is the production of methanol and n-butyl acetate by the transesterification reaction of methyl acetate and n-butanol. The n-butyl acetate is an important solvent in the chemical industry. It is used as a solvent for acrylic polymers, vinyl resins, and leather dressings in cosmetic formulations and other applications. It is also used as a reaction medium for adhesives. Methyl acetate is a byproduct of the poly-(vinyl)-alcohol production and has to be converted to methanol which is a feedstock of the poly-(vinyl)-alcohol production. First a feed of containing a low methyl acetate composition was first concentrated near to the methyl acetate/methanol azeotrope. A reactive distillation was added to convert methyl acetate by reacting with n-butanol into methanol and n-butyl acetate. Luyben, Pszalgowski, Schaefer, and Siddons proposed a three column design which converts feed stock containing 60 mol% of methyl acetate and 40mol% of methanol into methanol and n-butyl acetate[3].

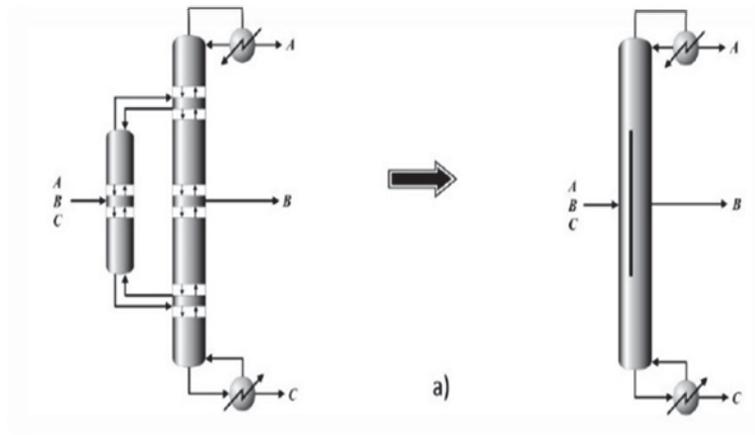


Fig.1 Thermally coupled system

In a reactive distillation column, a mixture of methanol and methyl acetate was reacted with a mixture of n-butanol and n-butyl acetate[3]. The top product containing methanol was recycled to a pre-fractionation column to mix with the fresh feed so that the overall feed composition falls between methanol and methyl acetate/methanol azeotrope. The bottom product containing n-butyl acetate and n-butanol was fed to a purification column to produce high purity n-butyl acetate and a mixture containing n-butanol and n-butyl acetate which was recycled to the reactive distillation column.

Linetal (2006) and Chen (2006) was used as the starting point of thermal coupling study[4]. A methyl acetate/methanol mixture, rich in methyl acetate, is fed to a reactive distillation column to react with n-butanol to produce a bottom product of n-butyl acetate. The top product is fed to a separation column to produce a distillate approximating the methyl acetate/methanol azeotrope, which is then recycled into the reactive distillation column. Methanol is recovered at the bottom of the separation column. The separation of multi-component mixtures by continuous distillation has traditionally been accomplished by arranging columns in series. Several alternative configurations exist, most notably the direct and indirect sequences. Thermal coupling between two columns in a sequence has proven to be very successful in providing energy savings around 30% with respect to the conventional distillation trains [5],[6]. However, their application was limited, mainly because of complexity in design and control of these structures [7]. In thermally coupled configurations at least one end of a distillation column has both liquid and vapor exchange with the other column. This eliminates either a reboiler or a condenser from the distillation column end. In three well known thermally coupled column configurations (side rectifier, side stripper, and fully coupled) for ternary separations, fully coupled configuration has been described to have higher thermodynamic efficiency for most separations [8]. However, [9] showed that the fully coupled configuration is favorable only in certain operating region. Side rectifier and side stripper configurations tend to provide the most thermodynamically efficient designs more often than the fully coupled configuration over a wide range of relative volatilities and feed compositions. In this study we will show that the reactive distillation process with thermal coupling for the production of high purity methanol and n-butyl acetate by reaction of methyl acetate and n-butanol cannot only save energy consumption but also have better operability and controllability than the conventional distillation process.

In this paper, we compared that specification products can be economically produced without the use of an extraction agent, by simulating system in ChemCad Software. Two alternative processes are explored: (1) 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 99.5% purity, and (2) a process with a reactive distillation with thermal coupling. In this thermo coupling process, the overhead of the reactive column is a methyl acetate/methanol mixture that is separated in a side column into a methanol as intermediate product and a distillate with a composition close to methyl acetate/methanol azeotrope, which is recycled back to the reactive distillation column. The bottom product of the side column is separated as butyl acetate and intermediate stream that is butanol/ butyl acetate azeotrope, which is recycled back to the reactive column. Fresh butanol with recycled butanol/ butyl acetate azeotrope and the methyl acetate fresh feed along with methyl acetate/methanol azeotrope streams are fed to the reactive column.

## II. CHEMICAL EQUILIBRIUM AND KINETICS

### A. The liquid-phase reversible reaction considered is



*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 Jimenez, Garvin, and Costa-Lopez (2002) [10] Ewa Bozek-Winkler and Jurgen Gmehling carried an experiment to predict the equilibrium data for the temperature range 104°F to 135°F [11]. 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 [11]. 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)[10], 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. CONVENTIONAL PROCESS

Fig.2 gives a sketch of the conventional process using Chemcad. In this flow sheet Fresh feed with a composition of 60 mol % methyl acetate and 40 mol % methanol and a flow rate of 128 lb-mol/h is fed to reactor, which operates at 200 °F. Fresh butanol (76.8 lb-mol/h) is also fed to the reactor, along with a butanol recycle stream and methyl acetate/methanol is recycled. Each column is operated at 15 psia, corresponding reflux ratio for columns are 1.5, 1.7, 2.8. Optimized value for above system is 61222.48 MJ/h.

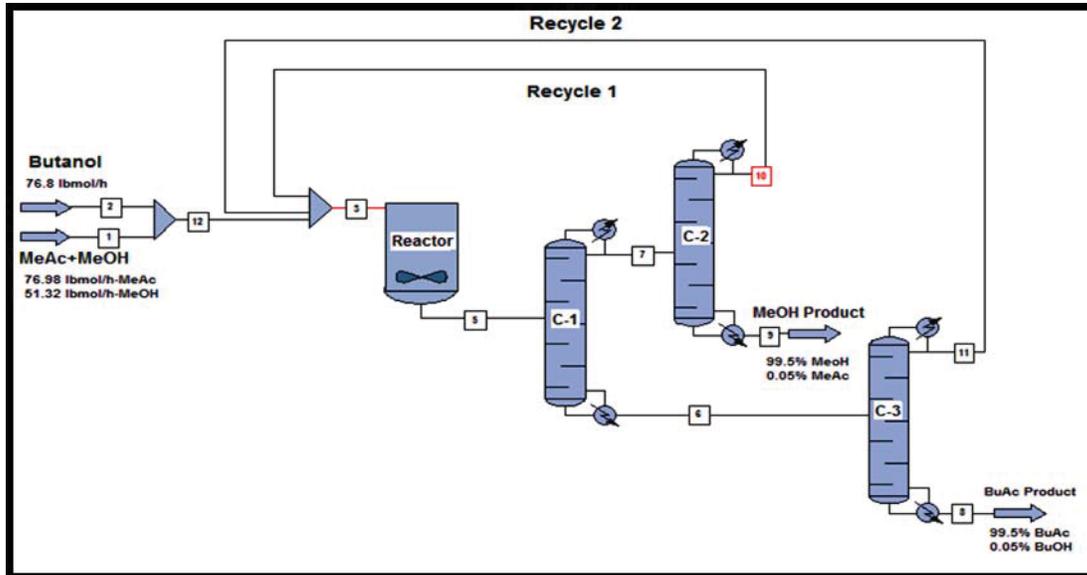


Fig.2- Flow sheet conventional process

#### IV. DESIGN OF REACTIVE DISTILLATION PROCESS WITH THERMAL COUPLING

The transesterification reaction of methyl acetate and *n*-butanol is proceeded as follows:



*n*-butyl acetate and methanol are the high and low boiling products, respectively. *n*-butanol and methyl acetate are the high and low boiling reactants, respectively. The yield for the transesterification reaction is strongly limited by the equilibrium conversion.

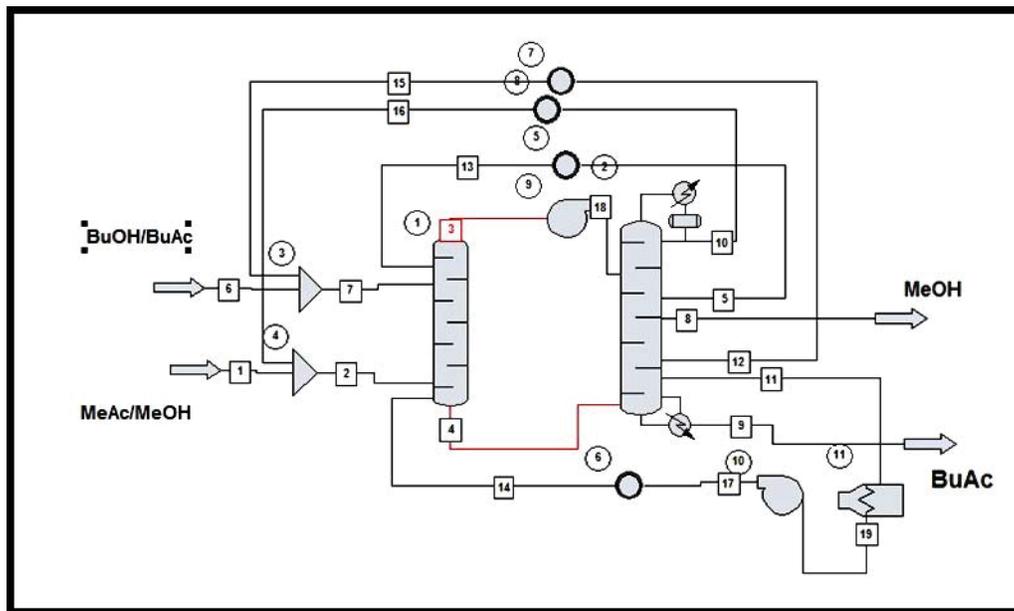


Fig 3- Thermal coupling reactive distillation process

In figure we show the flow sheet of a reactive distillation process with thermal coupling. The 27 number stages of a reactive distillation column and a side column with 55 number of stages are used in the study to compare the energy consumption of conventional distillation process with reactive thermal coupling. The same reaction volume on every tray in the reactive zone is used. Liquid and vapor are interchanged between these two units and then a condenser and reboiler and column are reduced. The *n*-butyl acetate is withdrawn from the side column as a bottom product. The approximate homogeneous azeotrope of methanol and methyl acetate is distilled at the column top and recycled back to the fresh methyl acetate feed location. A side draw is designed to purge from stage 18 as the methanol product from the side column. Its location is decided by selecting the tray with the maximum methanol composition. High purity butyl acetate with 99.5 mol% is obtained from the bottom of side column. There are four design degrees of freedom: reflux ratio and boil up flow of the side column, and liquid split ratio, number of stages used for reactive distillation process with thermal coupling. Liquid split ratio is specified as the ratio of the liquid flow directed to the side column to the flow directed to the reactive distillation column. In this study, reflux and liquid split ratios are used as the remaining degrees of freedom to minimize the reboiler duties of the reactive distillation process with thermal coupling while the other two are used to satisfy the purity specifications.

## V. RESULT AND DISCUSSIONS

Fig. 4 Shows the relationship between reboiler duty, reflux ratio and number of plates in second column when two product specifications are set at high purities (99.5mol %). The optimal condition with the minimum energy consumption (78500 MJ/h) is obtained with reflux and liquid split ratios equal to 6.8 and 0.36, respectively. A region with low energy consumption is observed for high liquid split ratio.

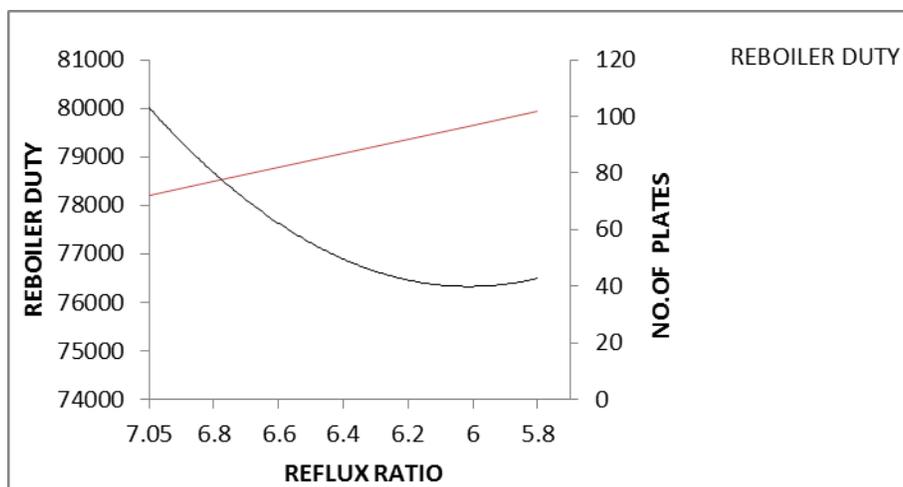


Fig. 4 - Optimum parameters for thermally coupled system

## VI. COMPOSITION PROFILES OF COLUMNS

In first column mixer feed is given to 7<sup>th</sup> and 21<sup>th</sup> stage. The region between 7<sup>th</sup> and 21<sup>th</sup> stage is reactive zone. Equal volume is maintained on each stage in reactive zone. After reaction in reactive zone, composition variation of first column is as shown in graph.

In side column bottom, product obtained as butyl acetate and methanol is as intermediate. Methanol is withdrawn from 40<sup>th</sup> stage. The composition variation in second column is as shown in graph.

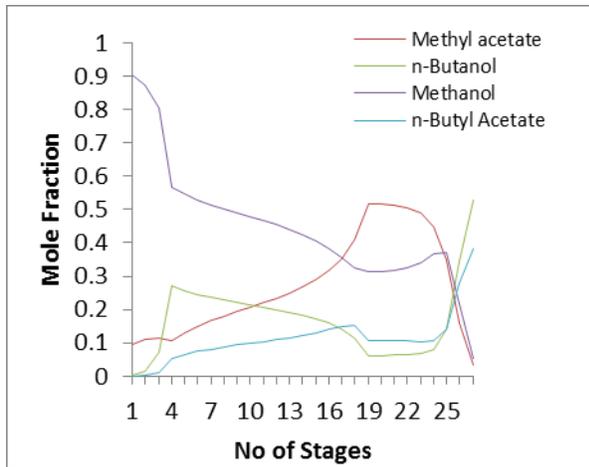


Fig. 5 Composition profile of first column.

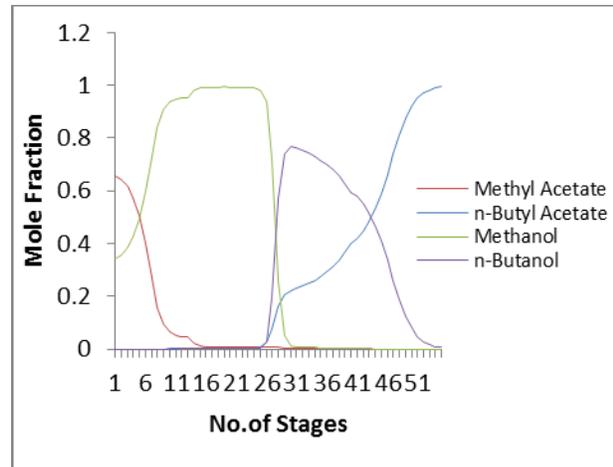


Fig. 6 Composition profile of second column.

## VII. EFFECT OF VARIATION IN REFLUX RATIOS AND FLOW RATES ON REBOILER DUTY

Figure 7 and 8 shows the reboiler duty profile with variation in flow rates and number of stages, which was directly obtained using plot function in Chemcad Software. In Fig 6, reboiler duty increases with increase in reflux ratio in coupled system. The variation in feed flow rate, how reboiler duty variation occurs is demonstrated in Fig.7.

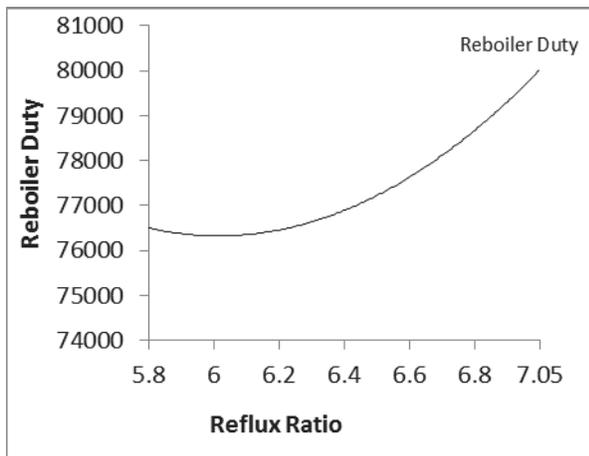


Fig. 7 Reflux Ratio Vs Reboiler Duty

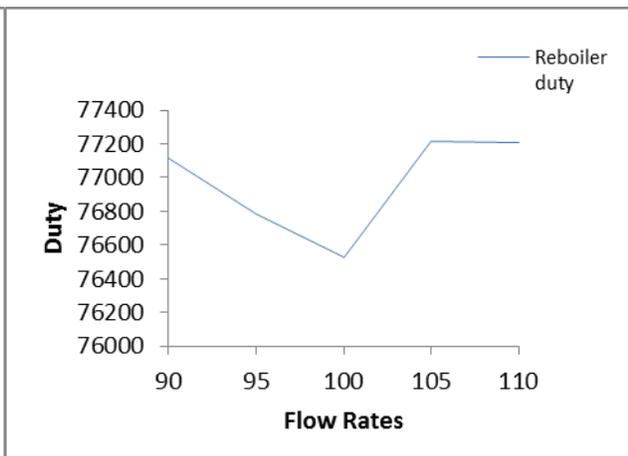


Fig. 8 Flow Rates Vs Reboiler Duty

## VIII. CONCLUSION

In the study, a reactive distillation process with thermal coupling is presented to produce *n*-butyl acetate and methanol by the transesterification reaction of methyl acetate and *n*-butanol. High product purities can be obtained at the bottom of side column of reactive thermally coupled distillation column. On comparing thermally coupled distillation system with conventional process, this system requires less number of columns which reduced capital cost. When systems are compared on basis of reboiler duty there is no significant difference.

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