Review Modeling of Reactive Distillation Column for the Production of Ethyl Acetate through Esterification

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Abstract: ***Reactive distillation is the combination of reaction and separation in a same column. It is an attractive option whenever liquid phase reactant is in large excess. The energy requirement of the conventional column is very high and requires large recycling costs. RD column works close to the stoichiometric feed conditions thereby eliminating recycling costs and increases the efficiency of the column. Reactive distillation is attractive when the liquid phase reactant is in large excess. The conversion of homogeneous and heterogeneous reaction takes place in reactive distillation column in which the reaction takes place in the presence of catalyst. Designing, operation and process development of RD column is highly complex task. Ethyl acetate and water is produced by the esterification of acetic acid and alcohol using catalyst such as sulphuric acid or ion exchange resins. The system temperature is kept at 70℃ and pressure of 1 atm. The reaction is endothermic, second order and reversible. Acetic acid and ethanol reacts according to the reaction to produce ethyl Acetate and Water. The reaction is highly equilibrium limited. The products are continuously sent to separation thus driving the equilibrium towards right direction. The process is non-ideal due to the presence of ethanol, acetic acid, ethyl acetate and water. There is the formation of five normal azeotropes i.e. ethanol-water, Water-acetic acid, ethyl acetate –ethanol, ethyl acetate-water, ethanol-acetic acid-ethyl acetate. Separation of these azeotropes is very difficult. In the proposed work review on modeling of the reactive distillation column for the production of ethyl acetate is given.***

Keywords: Reactive Distillation**, Et**hyl Acetate, Modeling, Endothermic, Mass-Balance.

1. Introduction

Ethyl Acetate is an important solvent widely used in many industries for the production of varnishes, ink, synthetic resins and adhesive agents it can be produced directly from ethanol (EtOH) and acetic acid (HAc) under acidic conditions. The reaction condition for the production of ethyl acetate is endothermic and there must be the low conversion of the reactants. This condition is very difficult to maintain and requires high capital investment and high energy costs. Thus Reactive distillation provides a good opportunity for the production of ethyl acetate. The key advantage for this is improved selectivity, increased conversion, heat integration benefits, lowers the economy by reducing the number of columns for separation operation and there is an avoidance of azeotropes in the reaction.

The Reactive distillation is the combination of reaction and separation in a single unit. The performance of the reactor is more than conventional and the sequential approach. In reactive distillation the performance of the reactor is increased due to the interest of researchers and scientists in this field. It is used more frequently in industries as much of the experimentation and research take place in this area.

There is no model and design available in literature that proves the usability of the process with its advantages. Most of the design process includes limitations and its simplified assumptions. None of the process deals with realistic model.

In-spite of number of models available in the literature, the entire model of a process depends on the intelligence of a researcher. The choice of correct feed location, reflux etc. The study of RD can be done in ways as: feasibility, simulation results, modeling and design, experimental process and pilot plant.

The modeling of RD column is very difficult task due to reaction and separation in the same column. The process of RD was first patented in 1920s and was commercialized on 1980s since Eastman Company owned and run a commercial process for the production of methyl acetate. Esterification, trans-esterification and hydrolysis reaction were firstly being studied in this process with homogeneous self-catalyzed reactions. Heterogeneous reaction in RD column was first studied in 1966 by spes in which the reaction takes place in the presence of a catalyst. The development of RD model was reviewed by taylor and Krishna in 2000.

2. Previous Work

Moses O.Tade et.al. (2003) provided a case study on ETBE by modeling a column and their significance on process development was discussed in “Modeling and control of reactive distillation systems”. They had developed and simulate RD column for the production of methyl acetate. An optimum value of reflux ratio is obtained with minimum number of stages. The equilibrium design of the process is verified with a kinetic simulation near operating conditions. The feasibility results are compared with the findings of bessling et. al. experimental results and were found very close to it.

JianjunPeng et. al. (2003) developed dynamic rate based and equilibrium based model of packed reactive distillation column for the production of tert-amyl methyl ether(TAME). Two models were developed, implemented in gPROMS, dynamic simulation was carried out and dynamic behavior of reactive distillation column for the production of TAME was studied. There was similarity in two models except some steady-state values.

Two models were developed for equilibrium based model and rate based model. Both the models are found to be same in there approximate values.

Muhamad Nazri Murat et. al. (2003) developed an equilibrium stage-wise reactive distillation model and process simulation was done. The algorithm for solving mathematical model was given by the set of differential-algebraic equations based on relaxation method. Simulation was performed on PC Pentium processor using a programming language in Fortran90. The results were validated from simulation result from the data in literature. The model so developed can give results on high isobutene conversion for the heterogeneous system as required for the industrial applications for the production of MTBE. The results were given in form of comparison on temperature profile, liquid composition profile and operating conditions of reactive distillation column. There work had shown promising results and the model to be used as a tool for the designing of reactive distillation column.

They had developed a model based on steady state simulation consists of number of ordinary differential equations and algebraic equations. Relaxation method is used for the solution of these equations. This method provides the better convergence of the equation and gives the solution to the equations. The model had provided the results as good as that of aspen plus simulation results.

Joe C. Thompson. et. al. (2004) prepared lab scale sieve tray RD column for the production of biodiesel in reactive distillation column. The experiment was developed for the trans-esterification reaction in the presence of a catalyst between vegetable oils and alcohol. The reaction was carried out in 100% excess of that required for the reaction to achieve maximum conversion to drive reversible process in forward direction in batch or continuous reactors.

The reactive distillation so developed has been found feasible for the production of biodiesel. The main objective of the study is reducing the alcohol to oil ratio. The study of the paper shows that the optimum temperature for the production of biodiesel is 66^{0}C with the molar ratio of 4:1 and a pre-reactor. The biodiesel obtained in this experiment meets the national standards (ASTM D 6751) for its viscosity and total glycerol.

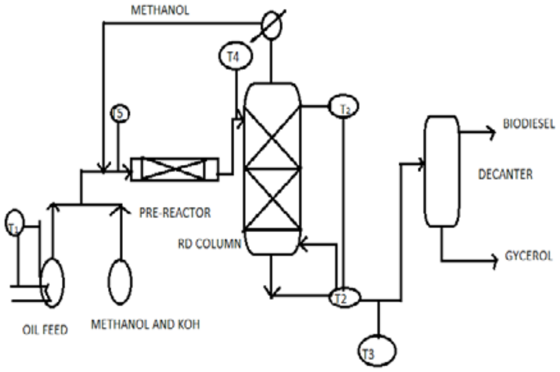

Figure 1: Production of Biodiesel in RD column

Myrian Schenk (2004) et. al. had studied a mixed-Integer Dynamic Optimization (MIDO) model In their study they developed a model and studied an integration between process operability and process modeling for the production of ethyl acetate. They had presented a feasibility of the model under certain bounded conditions for 17% to 20% savings over the design originally present in literature.

They had considered an advanced MIDO framework for process design, process control and the operability of the column. The result obtained is having a simultaneous approach rather than a sequential approach. The model developed by them is having a control system based on PI controller.

I-Kuan Lai et.al. (2008)Studied the production of ethyl Acetate in reactive distillation column and realizes the type-II reactive distillation column and also study the initial feed conditions to the column and a startup procedure for the continuous production of the product. The results are given for six experimental runs show that, by controlling the initial charges of the column, proper inventory hold ups and proper inventory conditions will increases the purity of ethyl acetate.

The paper shows an experimental study for the production of ethyl acetate of RD II process consists of a reactive distillation column, a stripper and the recycle. Six experimental runs with different initial feed conditions are run and showed that the performance of the reactor depends on the initial conditions.

Kwantip Konakom et. al(2010) had worked upon the purity of ethyl acetate to produce the product of approximately 90% pure. In the previous works ethyl acetate of 52% purity was achieved due to equilibrium limitations. The purity of the product is increased by installing many sequential units which requires large investments of the income.

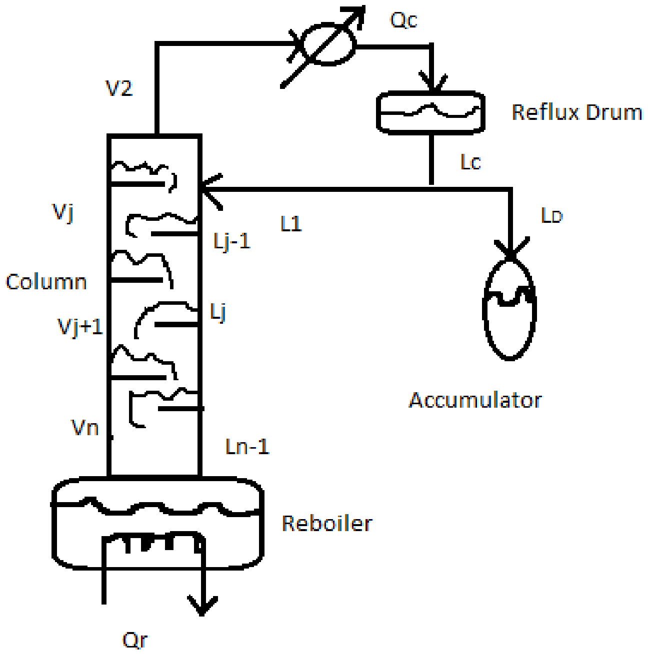

Figure 2: Model of RD column

So a batch column with reaction and separation in a single unit was proposed with the purity of 90% by mole. This purity cannot be achieved by constant reflux. Based on the open loop simulation the optimization problem is formulated for the product specification, re-boiler heat duty and batch operating time. The optimum reflux rate is achieved by optimizing the reflux starting with the minimum. The simulation of the process is done to obtain the purity of 90% by optimization programs.

Chokchai Mueanmas et. al. (2010) had developed a RD column for the production of Biodiesel. Earlier in conventional process alcohol was feed to the reactor in almost 100% excess which leads to large economic costs. Thus RD is used which drives the reaction towards the equilibrium and decreases the consumption of alcohol. They had studied on various parameters of the column to increase the rate of conversion and decrease the amount of alcohol.

They had concluded that the molar flow rate of 900ml/hr. re-boiler temperature of 90^0C, molar-ratio of 4:1 of methanol and alcohol with a residence time of 5 min. can give 92.70% biodiesel purity.

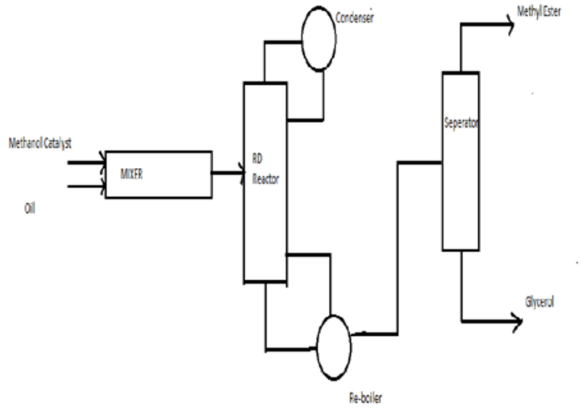

Figure 3: Biodiesel production process by RD

Ahmed D. Wiheeb et.al. (2011) they had provided RD column for the production of ethyl acetate and simulated it with the simulation tool HYSYS.

The reaction and separation takes place in the same column in a single column. The thermodynamic properties are calculated by Wilson, NTRL and UNIQUAC models which are available in HYSYS simulator programs. Effect of temperature at bottom product, reflux ratio and composition of water in the feed, effects of three feed conditions are studied (upper, split and middle). The results had shown that the best conditions are that the bottom conditions are at 83^0C-86^0C, reflux ratio at (2-5) with no water content in the feed and at split conditions. It was a successful simulation in HYSYS. The findings in the paper are that the most of the variables on the top of the column is not important. The water content in the feed is reduced leading to less efficiency of the tower and hence the production of EtAc is reduced.

The simulation of the process is done and the best operating conditions are found to be: The bottom temperature of the column is 85-87^0C. The best feed conditions are found as the split feed conditions. The molar reflux is in range of 2-5. Wilson model was accepted as the best model for the calculation of all thermodynamic properties.

Nghi Nguyen and co-workers in 2011 had worked upon the production of ethyl dodeconoate using lauric acid and methanol with a solid catalyst of sulfated zirconia is studied. They had studied this system in two ways: In the first system methanol recovery column followed the distillation column and in other the thermally coupled methanol recovery and reactive distillation column was designed. The thermal recovery column consumes less energy. This is done by inter connection liquid and vapor streams thus eliminating the re-boiler and condenser. The distillation sequences is optimized and found that there is 13.1% of less energy requirement as in reactive distillation column and the recovery of the methanol was increased by 50%. The energy loses in the column is reduced by 281.35 kW which is 21.7% of the available energy required. In addition to it the composition of the column was also improved. There is less water required as that of original water content which decreases the deviation of the catalyst during the reaction.

This work improves the energy requirement in the column. Thus the capital investment and the operating cost have reduced as that of the conventional reactive distillation sequence. This has also decreases the energy required in liquid-liquid extraction for the separation of the methanol and protects the catalyst from deviation.

Luisa F. Rios et. al. (2012) had developed a model in aspen plus 7.2 for the production of biodiesel from soya-bean oil and ethanol in the presence of the catalyst. The experimental studies say that the best biodiesel composition was found at 1.34% of catalyst and ethanol with a molar ratio of 8:1. The experiment was found to be in good review because all the process variables are carefully evaluated. The simulation of the process is done to evaluate other variable and optimization of the process is done. This study had showed that using pre-reactor before the column increases the efficiency of the column. The software for the simulation had provided same as experimental results with slight variations.

Abdulwahab Giwa (2012) had developed a dynamic model for the production of Ethyl acetate. The modeling for the production of ethyl acetate was been compared with the experimental work. The major parameters considered in the work are top and bottom temperatures. The model considered in the experiment was a column in which reaction takes place in the presence of amberlyst catalyst-15 while the rectification and stripping sections are both filled with rashing rings. The dynamic model was developed with first principle was solved in MATLAB R2011a.

The results of the experiment are compared with that of the simulation results and were found in good agreement with very small residual errors.

Raul Delgado et.al.(2012) have worked upon the control and design of the thermally coupled distillation sequences using a single shell divided by a wall named divided wall distillation column. In this work the production of ethyl acetate in a divided wall distillation column was done for the first time. The simulation of the process was done in aspenONE aspen plus. The results obtained in the process are in good agreements of that of the simulation results.

The work, startup and the operation of the column to carry out esterification reaction was successfully done. The results obtained are compared with the simulation results and corroborated by gas chromatography.

Priyanka Gautam et. al. (2013) had done modeling and simulation of RD column for the production of ethyl acetate in Aspen Plus. The effect of feed temperature and composition was studied by varying the feed flow rates.

3. Conclusion

The modeling of RD column for the production of ethyl acetate through esterification was reviewed in this paper. The study had showed that the model developed are based on various assumptions thus shows deviations from the experimental data. The thermodynamics of liquid phase activity coefficient controls the modeling of the process. However user based models provides the best results.

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